STATISTICAL PHYSICS

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PREFACE

THE aim of this book is to give a unified presentation of thermodynamics and classical statistics, based on the point of view associated with the name of Gibbs.

No attempt has been made at mathematical rigour in the treatment, since this is anyhow illusory in theoretical physics, but we have instead tried to make clear the fundamental physical assumptions on which the results are based. We cannot claim to have succeeded in this everywhere, and no doubt the reader will find that the physical bases of some of the results are not completely founded.

The treatment of § 41 is based on the work of Onsager,† that of § 72 on the work of Wagner and of Schottky,‡ and that of §§ 70, 71, and the whole of Chapter XI in general, is based on the work of Landau.||

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† Onsager, *Phys. Rev.* **37**, 405, 1931; **38**, 2265, 1931.
‡ Wagner and Schottky, *Z. f. phys. Chem.* **B**, **11**, 163, 1930.
|| Landau, *Phys. Zeit. d. Sow. Union*, **8**, 113, 1935; **11**, 26, 545, 1937.

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I

INTRODUCTION

1. Probability

SYSTEMS with a small number of degrees of freedom, such as the planets in the gravitational field of the sun or rigid bodies, can be studied by the methods of classical mechanics. By constructing the equations of motion of the system (as many as there are degrees of freedom) and integrating them, complete information about the motion of the system can be deduced.

When, however, we have to deal with systems which, although obeying the laws of classical mechanics, have a very large number of degrees of freedom (for instance, macroscopic bodies consisting of say 10^{25} particles), the number of equations of motion becomes too large to solve in practice. The mathematical difficulties become so immense in fact, that in a sense we can consider the solution as impossible in principle as well as in practice. Even if it were possible to integrate the equations of motion, it would be quite impossible to insert the initial conditions for the velocities and coordinates of all the particles into the general solution, if only for lack of time and paper.

These considerations might at first sight suggest that as the number of degrees of freedom increases, the properties of a mechanical system should become more and more complicated, and that it should become increasingly difficult to find any regularity in its behaviour. Fortunately this is not true, and we shall see that just when there is a very large number of degrees of freedom the system obeys laws of a special kind. The investigation of these laws forms a special branch of theoretical physics, called *statistical physics*, or as we shall say more briefly *statistics*, which is of considerable importance because the systems actually occurring in nature often have so many degrees of freedom that they can be treated only by statistical methods.

In statistical physics we have to introduce a number of new concepts, which do not occur in ordinary mechanics, and of these the most fundamental is the idea of probability, which we shall discuss first of all. Consider a physical system in constant external conditions, which can in general be in one of a number of states, and makes

transitions from one state to another with the passage of time. Each state can be described by specifying the particular values which certain characteristic parameters of the system assume in that state.

Suppose now that we carry out a series of measurements from which we can deduce the values of the characteristic parameters at some instant, and so find out in which particular state the system was at that instant. From a number of such observations we can then write down the number of times the system was observed in some particular state. The ratio of the latter number to the total number of observations is found to approach a certain limit for each state as the total number of observations is increased, and this limit is called the *probability* of the state.

If the observations are carried out during sufficiently short equal intervals of time, the time spent by the system in any state will be proportional to the number of observations in which it is found in that state. Thus the probability w_A of a state A can be defined as the limit of the ratio of time t_A spent by the system in state A to the total time T of observation, as T becomes very large:

$$w_A = \lim_{T\to\infty} t_A/T. \tag{1.1}$$

If two states A and B have probabilities w_A and w_B we can deduce the joint probability of the two states, i.e. the probability that the system is in either of these states. The total time spent by the system in either state is obviously the sum of the times spent in each separately, and consequently the joint probability is the sum of the separate probabilities, w_A+w_B. Similarly, the total probability of any number of states is the sum of their separate probabilities. This simple result is known as the *theorem of addition of probabilities.*

By applying this theorem to *all* the possible states of the system we see that the sum of the probabilities of all the states must be unity (which follows also directly from the definition (1.1)). Thus we have

$$\sum_A w_A = 1. \tag{1.2}$$

This equation is called the *normalization condition.*

We mentioned earlier that a state is described by the values of certain parameters characteristic of it, and so we can regard the probability of a state as the probability that the parameters have the particular values appropriate to that state. We may, however, be

interested only in some, and not all, of the parameters specifying the state. Suppose for instance that a state is described by two parameters L and M, and w_{LM} is the probability that these parameters have some particular values, then to find the probability that one of these parameters, L say, has a particular value, we must, by the addition theorem, add together the probabilities of all the states with this value of L, i.e. sum w_{LM} over all possible values of M:

$$w_L = \sum_M w_{LM}. \tag{1.3}$$

So far we have assumed that the system has only a discrete series of possible states, but the above considerations can easily be generalized to the case usually occurring in practice of a continuous series of states, that is to say, the case where the characteristic parameters can assume a continuous series of values. We then have to introduce the probability $dw(A)$ of some interval of states, dA, and the normalization condition (1.2) becomes

$$\int dw(A) = 1, \tag{1.4}$$

the integration being extended over all possible states.

The probability $dw(A)$ of an interval dA is usually written in the form $\rho(A)\,dA$, so that $\rho(A)$ is roughly speaking the probability of unit interval of state and can be called the *probability density*.

The normalization condition is then

$$\int \rho(A)\,dA = 1. \tag{1.5}$$

2. Mean values

Consider again the series of measurements described in § 1 and suppose that we determine the value of some quantity M which depends on the state of the system. The various measurements will in general give rise to different values corresponding to the changes of state with time. The *mean value* of M is then defined as the limit of the sum of all the values obtained, divided by the total number of measurements, when this number is indefinitely increased.

In the construction of this sum the value M_A of M corresponding to the state A is multiplied by the number of measurements in which the system is found in this state, and so, after dividing by the total number of measurements and going to the limit, M_A is multiplied by the probability of the state A. Thus the mean value of M is the sum for all possible states of the products of the values of M and the

corresponding probabilities. Denoting the mean value by $\bar{M}$, we have then

$$\bar{M} = \sum_A M_A w_A. \tag{2.1}$$

By a similar argument the mean value of M for a continuous series of states is

$$\bar{M} = \int M(A)\rho(A)\,dA. \tag{2.2}$$

Two simple theorems on the evaluation of means follow from these results. If two quantities L and M are functions of the state of the system, then by (2.1) the mean value of $L+M$ is

$$\overline{L+M} = \sum_A w_A(L_A+M_A) = \sum_A w_A L_A + \sum_A w_A M_A = \bar{L}+\bar{M}, \tag{2.3}$$

i.e. *the mean of a sum is the sum of the separate means* (a similar proof holds for the case (2.2) of a continuous series of states). Again, if M is a function of state and α some constant quantity, the mean value of αM is

$$\overline{\alpha M} = \sum_A w_A \alpha M_A = \alpha \sum_A w_A M_A = \alpha\bar{M}. \tag{2.4}$$

The quantity M assumes values differing from $\bar{M}$ as the state of the system changes with time, and we shall now introduce a quantity to describe the average width of the interval in which M varies about its mean value. For this purpose the average value of $(M-\bar{M})$ is obviously of no use, because even though M may often differ considerably from $\bar{M}$ the difference is sometimes positive and sometimes negative, and the mean of $(M-\bar{M})$ is in fact just zero. It is, however, convenient to take as the characteristic quantity the mean value of the *square* of the difference, i.e. $\overline{(M-\bar{M})^2}$. Since $(M-\bar{M})^2$ is always positive its mean can be zero only if $M-\bar{M}$ is *always* zero, and more generally $\overline{(M-\bar{M})^2}$, which is $\sum_A w_A(M_A-\bar{M})^2$, is small only if large deviations of M from $\bar{M}$ have small probabilities.

Denoting the difference $M-\bar{M}$ by ΔM, and remembering that $\bar{M}$ is a constant independent of the state, we find from (2.3) and (2.1)

$$\overline{(\Delta M)^2} = \overline{M^2-2M\bar{M}+\bar{M}^2} = \overline{M^2}-(\bar{M})^2.$$

The quantity $\sqrt{\overline{(\Delta M)^2}}$ is known as the *fluctuation*† of M, and the ratio of this fluctuation to the mean value $\bar{M}$ is called the *relative fluctuation*. It will be seen that the smaller the relative fluctuation, the smaller is the time spent by the system in states for which the deviation of M from $\bar{M}$ is an appreciable fraction of $\bar{M}$.

† We shall, however, often use the word fluctuation for $\overline{\Delta M^2}$ (i.e. for the square of the fluctuation here defined) when there is no possibility of confusion.

3. Statistical independence

We shall now consider a number of independent systems, independent in the sense that there is no interaction between them, so that the state of any one system has no influence on the probabilities of the various states of the other systems. Such systems may be at the same time independent parts of a more complicated system.

Let A be some state of one of the systems with probability w_A, and B a state of another system with probability w_B. Consider now the compound system made up of the two systems together, and the probability of the state AB, for which, simultaneously, the first part (i.e. one of the independent systems) is in state A, and the other is in state B. If T is a sufficiently long interval of time, then in the course of this interval the first part will spend a time $w_A T$ in state A, by definition of w_A. If T is taken so large that $w_A T$ is itself a sufficiently long interval, then in the course of this latter interval the second part will spend a time $w_B w_A T$ in state B. Thus the two parts of the compound system are respectively in states A and B simultaneously during a fraction $w_A w_B$ of the total time, and therefore the probability of the state AB is the product of the probabilities of A and B. This result is known as the *theorem of multiplication of probabilities* and can be easily extended to any number of independent systems.

Conversely, if the probability of any state of a complex system can be expressed as a product of factors, each depending on quantities describing only a single part of the system, then these parts must be independent in the sense explained above, and each factor gives the probability of a state of the corresponding part.

For the case of a continuous series of states, let dA be an interval of states of one of the independent systems and dB an interval of states of the other. If $w(A)\,dA$ and $w(B)\,dB$ are the corresponding probabilities, then the probability that the two systems should be simultaneously in these intervals is $w(A)w(B)\,dA\,dB$. Considering $dAdB$ as an interval of states of the complex system, we obtain the multiplication theorem for probability densities.

By means of the multiplication theorem we can find the mean value of the product LM of two functions of the states of independent systems (L being independent of the state of one of the systems and M of the state of the other). Thus

$$\overline{LM} = \sum_{AB} w_A w_B L_A M_B = \sum_A w_A L_A \sum_B w_B M_B = \bar{L}\bar{M}, \qquad (3.1)$$

or *the mean of the product of independent quantities is the product of the separate means.*

Let us now determine the fluctuation of the sum of two independent quantities. This is evidently

$$\overline{\{\Delta(L+M)\}^2} = \overline{(\Delta L+\Delta M)^2} = \overline{(\Delta L)^2}+\overline{(\Delta M)^2}+2\overline{\Delta L\,\Delta M}.$$

Now since L and M are independent quantities we can apply the multiplication theorem to the last term:

$$\overline{\Delta L\,\Delta M} = \overline{\Delta L}\,\overline{\Delta M} = 0,$$

since $\overline{\Delta L}$ and $\overline{\Delta M}$ are each zero as was mentioned in § 2. Thus

$$\overline{\{\Delta(L+M)\}^2} = \overline{(\Delta L)^2}+\overline{(\Delta M)^2}, \tag{3.2}$$

and a similar result holds for any number of independent quantities.

Suppose that some system consists of a large number N of identical independent parts, and let M be some function of the state of the system. Suppose further that M is an additive quantity, by which we mean that its value M for the whole system is equal to the sum of its values M_i ($i = 1, 2,..., N$) for each of the independent parts, i.e. $M = \sum_{i=1}^{N} M_i$, then by (2.3) the same must be true of the mean value, i.e.

$$\bar{M} = \sum_{i=1}^{N} \overline{M_i}.$$

From (3.2) we see that the fluctuation of M may be written as

$$\overline{(\Delta M)^2} = \sum_{i=1}^{N} \overline{(\Delta M_i)^2}.$$

With increase of N, this sum increases proportionally to N, i.e. the absolute fluctuation $\sqrt{\overline{(\Delta M)^2}}$ is proportional to $\sqrt{N}$. Now $\bar{M} = \sum_{i=1}^{N} \overline{M_i}$ is obviously proportional to N and we see, therefore, that the relative fluctuation is inversely proportional to $\sqrt{N}$, so that *with increase of the number of independent component parts, the relative fluctuation of all physical quantities, whose values for the whole system are the sums of their values for the separate parts, becomes smaller*, and if the number of parts is sufficiently great the values of these physical quantities for the whole system can in fact be considered as constant, equal to their mean values. This result will play an important role in what follows.

II

STATISTICAL DISTRIBUTION AND ENTROPY

4. Statement of the problem

We shall now consider a mechanical system with a very large number of degrees of freedom, such as any real macroscopic body, and we shall suppose the system to be *closed* in the sense that there is no interaction between it and any other bodies.

If the number of degrees of freedom of the system is sufficiently great, a part of the system although small in comparison to the whole will itself still have a large number of degrees of freedom. This part, which we shall call a *subsystem*, forms a new mechanical system, but no longer a closed one, since it can interact with the remaining parts of the original closed system. Owing to the great number of degrees of freedom of these other parts, the interactions will be very complicated and correspondingly the state of the subsystem will vary with time in a very complicated manner.

The problem of the behaviour of the subsystem can be treated *exactly* only by solving for the whole system all the differential equations of motion for the given initial conditions, and this, as we saw in § 1, is an impossible task. Fortunately, however, the very complication of the variations of state of the subsystem which prevents the application of mechanical methods, allows an approach to the problem from a different point of view.

In fact, just because of the extreme complication of its interaction with the remainder of the system, the subsystem will, in a sufficiently long time, pass through every interval of the possible series of states (supposed continuous) several or even many times. The probability of any such interval of states can be described by a continuous function whose value is determined by how often the subsystem passes through the interval, or by how long a time it spends in the interval during a given time. Evidently the replacement of the complicated variation of state by a continuous function can be only approximate, but the approximation becomes more exact, the greater the number of degrees of freedom of the whole system. This continuous function (which is the same as the probability density (§ 1)) is called the *statistical distribution* or *distribution function* for the subsystem concerned.

This distribution function will not depend on the initial state of any other small part of the whole system, since the influence of this initial state will in a sufficiently long time be outweighed by the influence of the other much larger parts of the whole system. In the same way it will be independent of the initial state of the subsystem itself, since in the course of time the subsystem passes through all its possible states, any one of which could be chosen as the initial one.

It is this property of a system with a large number of degrees of freedom which permits the determination of the distribution function without solution of the mechanical problem for given initial conditions, and, in fact, *the determination of the distribution function of a relatively small part of a macroscopic system is a problem of statistics.*

Once the distribution function is known, the probability of any given value of a quantity which is a function of the state of the subsystem can be determined. Conclusions made from statistics in this way have a 'probability' character, this being connected with the fact that much fewer data are necessary to obtain them than in the corresponding mechanical problem, and in this respect they differ from the strictly deterministic results of classical mechanics.

If the subsystem is itself a macroscopic system, we can apply the result of § 3, that the relative fluctuation of physical quantities associated with a system falls rapidly with increase of the size of the subsystem, and we obtain the remarkable result that *over sufficiently long times the physical quantities associated with a macroscopic system remain, on the average, practically constant* (*equal to their mean values*), and appreciable deviations from the mean values occur relatively seldom. In other words the probability of different states of the system has a sharp maximum for those states for which the physical properties of the system have their mean values.† Thus in calculating the mean values of such physical quantities, whose relative fluctuations are small, statistics makes predictions which are true to a very high order of approximation for an overwhelming proportion of any sufficiently long time. In this sense *the predictions of statistics assume a practically deterministic instead of a probability character.*

If a closed macroscopic system is in such a state that for each of its subsystems additive physical quantities are with great relative

† For this reason we shall often omit the averaging sign when referring to mean values.

accuracy equal to their mean values, it is said to be in a state of *statistical equilibrium*, and from the above consideration it is evident that for a large proportion of a sufficiently long time the closed system will indeed be in a state of statistical equilibrium. If at some moment the closed system is not in a state of statistical equilibrium (if, for instance, it was taken out of this state by external means, and then left to itself, i.e. again became closed), then it will return to statistical equilibrium at some later time. The time required for return to statistical equilibrium is called the *relaxation time*, and the study of processes associated with the return forms the subject of *kinetics* as distinct from statistics in the narrow sense, which deals with systems in statistical equilibrium and to which this book is confined.

5. Phase space. Liouville's theorem

As a preliminary to the discussion of the statistical distributions of macroscopic systems, we must first of all introduce the idea of *phase space*, which we shall require in what follows.

If the macroscopic system has n degrees of freedom, then to describe the position of the system at any moment we need to know the appropriate values of n parameters called the generalized coordinates, denoted by q_i ($i = 1, 2, \ldots, n$). The state of the system at that moment is then determined by the instantaneous values of the n coordinates q_i and the corresponding velocities $\dot{q}_i$, both of these being in general functions of time.

In statistics it is more usual to specify the state by the coordinates and *momenta* (p_i) instead of velocities, as this has several important advantages. The various states of the system can be represented by points in the so-called *phase space* (which is, of course, nothing more than a convenient mathematical fiction), in which the coordinates of any point represent the coordinates and momenta corresponding to a particular state. Thus every system has its own phase space of a number of dimensions twice that of the number of degrees of freedom. In the course of time the representative point in phase space describes some curve, called the *phase trajectory*, corresponding to the changes of state of the system.

The probabilities of the various states will be given by a function of the coordinates and momenta, and since all the coordinates and momenta can assume a continuous series of values, the states of the system are also a continuous series, and we have to speak of the

probability of an interval of states. We have already used this idea earlier, and we can now define the probability of an interval

$$dq_1\, dq_2 \ldots dq_n\, dp_1\, dp_2 \ldots dp_n$$

more precisely as the probability that the coordinates and momenta have values between

$$q_1,\ldots, q_n; p_1,\ldots, p_n \quad \text{and} \quad q_1+dq_1,\ldots, q_n+dq_n; p_1+dp_1,\ldots, p_n+dp_n.$$

Geometrically this can be expressed as the probability of finding the representative point in phase space within an element of 'volume' of phase space $d\Gamma = dq_1 \ldots dq_n\, dp_1 \ldots dp_n$. As explained in § 1 this probability can be written as

$$dw = \rho(q_1,\ldots, q_n; p_1,\ldots, p_n)\, d\Gamma,$$

where $\rho(q_1 \ldots, q_n; p_1 \ldots, p_n)$† is a function of all the coordinates and momenta, playing the role of probability density. Our problem is to determine this distribution function ρ for a macroscopic system in statistical equilibrium.

The normalization condition (1.5) now becomes

$$\int \rho(p, q)\, d\Gamma = 1,$$

the integration being extended over all accessible phase space.‡ The mean value of any physical quantity $M(p, q)$ which is a function of the coordinates and momenta of the system is by (2.2)

$$\bar{M} = \int M(p, q)\rho(p, q)\, d\Gamma. \tag{5.1}$$

If we consider some region in the phase space of a system, then each point in this region represents a state of the system, and in the course of time moves along a line as determined by the equations of motion of the system. In this way, after some time, the region concerned (i.e. the assembly of points in the region) will have moved into another region of phase space.

The initial 'volume' of this region may be written as $\int\limits_{\gamma_0} d\Gamma_0$, where $\int\limits_{\gamma_0}$ means integration over the region concerned. After time dt, a point which had coordinates $q_{10},\ldots, q_{n0}; p_{10},\ldots, p_{n0}$ will have moved to the new position $q_1,\ldots, q_n; p_1,\ldots, p_n$, where

$$q_1 = q_{10}+\dot{q}_{10}\, dt,\ldots; \qquad p_1 = p_{10}+\dot{p}_{10}\, dt,\ldots,$$

† We shall often use the abbreviation $\rho(p, q)$ or simply ρ for this function.

‡ By this we mean that the integration is extended over only those parts of phase space for which the coordinates and momenta have admissible values, e.g. if the system is confined to a finite volume, the integration with respect to coordinates is confined to coordinates of points within this volume.

and the volume of the new region occupied by the points will be $\int_\gamma d\Gamma$, where $d\Gamma = dq_1 \ldots dq_n\, dp_1 \ldots dp_n$, and the integration is extended over the new region. Now the change from $\int_{\gamma_0} d\Gamma_0$ to $\int_\gamma d\Gamma$ can be regarded simply as a transformation of variables from

$$q_{10},\ldots,q_{n0};p_{10},\ldots,p_{n0} \quad \text{to} \quad q_1,\ldots,q_n;p_1,\ldots,p_n,$$

and so by the well-known properties of multiple integrals

$$\int_\gamma d\Gamma = \int_{\gamma_0} \frac{\partial(q_1,\ldots,q_n;p_1,\ldots,p_n)}{\partial(q_{10},\ldots,q_{n0};p_{10},\ldots,p_{n0})}\, d\Gamma_0,$$

where $\frac{\partial(q_1,\ldots,q_n;\,p_1,\ldots,p_n)}{\partial(q_{10},\ldots,q_{n0};\,p_{10},\ldots,p_{n0})}$ is the Jacobian† of the transformation. We shall next prove that the differential coefficient of the Jacobian with respect to time, i.e. $\frac{d}{dt}\frac{\partial(q_1,\ldots,q_n;\,p_1,\ldots,p_n)}{\partial(q_{10},\ldots,q_{n0};\,p_{10},\ldots,p_{n0})}$, is zero, from which it follows that the Jacobian is constant and must in fact be unity since it was unity initially. For simplicity of proof we shall suppose here that there is only one momentum component p and one coordinate q, the general proof being completely analogous.

By equation (v) of the footnote we may write

$$\frac{d}{dt}\frac{\partial(q,p)}{\partial(q_0,p_0)} = \frac{\partial(\dot{q},p)}{\partial(q_0,p_0)} + \frac{\partial(q,\dot{p})}{\partial(q_0,p_0)}.$$

† The Jacobian $\frac{\partial(u,v)}{\partial(x,y)}$ is defined as

$$\frac{\partial(u,v)}{\partial(x,y)} = \begin{vmatrix} \frac{\partial u}{\partial x} & \frac{\partial u}{\partial y} \\ \frac{\partial v}{\partial x} & \frac{\partial v}{\partial y} \end{vmatrix}. \tag{i}$$

It has the following obvious properties

$$\frac{\partial(u,v)}{\partial(x,y)} = -\frac{\partial(v,u)}{\partial(x,y)}, \tag{ii}$$

$$\frac{\partial(u,y)}{\partial(x,y)} = \left(\frac{\partial u}{\partial x}\right)_y. \tag{iii}$$

The following relations can also be easily shown to hold:

$$\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial(u,v)}{\partial(s,t)}\frac{\partial(s,t)}{\partial(x,y)}, \tag{iv}$$

$$\frac{d}{dt}\frac{\partial(u,v)}{\partial(x,y)} = \frac{\partial\{(du/dt),v\}}{\partial(x,y)} + \frac{\partial\{u,(dv/dt)\}}{\partial(x,y)}. \tag{v}$$

The first of these Jacobians can be expressed in the form

$$\frac{\partial(\dot{q},p)}{\partial(q_0,p_0)} = \frac{\partial(\dot{q},p)}{\partial(q,p)}\frac{\partial(q,p)}{\partial(q_0,p_0)} = \frac{\partial\dot{q}}{\partial q}\frac{\partial(q,p)}{\partial(q_0,p_0)}$$

(see equations (iii) and (iv) of the footnote on p. 11), and similarly for the second Jacobian. Thus we have

$$\frac{d}{dt}\frac{\partial(q,p)}{\partial(q_0,p_0)} = \left(\frac{\partial\dot{q}}{\partial q}+\frac{\partial\dot{p}}{\partial p}\right)\frac{\partial(q,p)}{\partial(q_0,p_0)}.$$

Now it is easy to see that the expression in brackets is exactly zero, for p and q must satisfy Hamilton's equations

$$\dot{q} = \partial H/\partial p, \qquad \dot{p} = -\partial H/\partial q,$$

where H is the Hamiltonian function for the given system.

So $$\frac{\partial\dot{q}}{\partial q} = \frac{\partial^2 H}{\partial q\partial p} = -\frac{\partial\dot{p}}{\partial p} \quad\text{and}\quad \frac{\partial\dot{q}}{\partial q}+\frac{\partial\dot{p}}{\partial p} = 0.$$

We have thus proved the remarkable theorem first obtained by Liouville that

$$\int_\gamma d\Gamma = \text{constant}, \tag{5.2}$$

where the integration refers of course not to a definite fixed part of phase space, but to a mobile region occupied by the points in the initially chosen region. *Every volume of phase space remains unchanged in size during the motion it carries out corresponding to changes of state of the system.*

6. The role of the energy

The subsystems discussed in § 4 are not of course closed systems themselves, but since, although small compared with the whole system, they still have many degrees of freedom, they also may be considered as macroscopic systems and can be treated as 'quasi-closed' in the sense that during any not too long time they behave approximately as if they were closed.

The justification for this statement is that the interaction with the rest of the system is a surface effect in the sense that it arises from only those parts of the subsystem close to its surface, while the interaction of all the individual parts of the subsystem with each other is a volume effect since it involves *all* the parts of the subsystem. Thus if the subsystem is sufficiently large its external interactions will be small compared with its internal interactions, since volume effects increase more rapidly than surface effects with increase of dimensions.

The basic condition for a subsystem to be quasi-closed (or quasi-independent) is that its interactions with the remainder of the main system are relatively weak, and this may sometimes be satisfied even if the subsystem is small in itself, provided its external interactions are relatively weak for other reasons (see for instance § 20, the case of a perfect gas).

In these conditions all quantities of physical interest are approximately additive. For instance, since the internal energy of a subsystem is, as we saw above, much larger than its interaction energy with the rest of the system, the total energy of the whole system is approximately the sum of the energies of its component subsystems.

We can now return to our problem of determining the distribution function, and in order to do this, we again consider a part of the closed macroscopic system, small compared with the whole system, but large enough to have a great number of degrees of freedom, i.e. forming a macroscopic system in itself. Consider some sufficiently long time and suppose it divided into a large number of equal intervals corresponding to successive instants $t_1, t_2, \ldots$. At each of these instants the subsystem concerned is represented by a point in its own phase space, and the whole assembly of points corresponding to the instants $t_1, t_2, \ldots$ is distributed in phase space in such a way that the number of points in an element of phase volume is proportional to the distribution function $\rho(p, q)$ in that element. This statement is of course only approximate, but becomes more exactly true the longer the whole interval of time or the shorter the intervals between the successive instants of time.

An alternative point of view is to introduce an assembly of identical systems which, at a given moment, are in each of the states through which our actual subsystem passes at the instants $t_1, t_2, \ldots$. In other words instead of examining the states of the same subsystem at various instants, we can examine simultaneously an assembly of identical systems in various states, whose representative points are distributed in phase space according to the distribution function appropriate to the actual subsystem concerned.

After a time t, the states of all these systems will have changed according to the equations of mechanics, and the new states (which coincide with those of the actual subsystem at instants $t_1+t, t_2+t, \ldots$) will be represented by an assembly of points in phase space, distributed with a density proportional to $\rho(p, q)$, which is of course

the *same* function as for the original assembly of points. Thus the distribution function of a quasi-closed system is *stationary*, or in other words the points in phase space representing our assembly of systems (or representing the same subsystem at different instants) move about in such a way that their density at any place remains proportional to $\rho(p, q)$.

Consider those points in phase space (representing states of the systems, i.e. states of the original subsystem at instants $t_1, t_2, \ldots$) which lie within some region A. After some time all the points in A will have moved into some new region B following trajectories which correspond to the mechanical equations, and by Liouville's theorem A and B must be of equal volumes. This means that the density of points is the same in A and B, and since the density is proportional in each case to $\rho(p, q)$ at the appropriate place we deduce the important result that *the distribution function is constant along the phase trajectory* which represents the change of state of the system.

From this it follows immediately that ρ can depend only on such quantities (functions of coordinates and momenta) which are constant along the trajectory, i.e. which remain constant during the motion. As is well known from mechanics these so-called invariants of motion are the first integrals of the equations of motion (a system with n degrees of freedom has $(2n-1)$ invariants); we can therefore say that the distribution function, since it is a function only of the invariants of motion, is itself an invariant of motion. Since there are in all $2n$ variables of which ρ can be a function (the n coordinates and n momenta), this is of course not at all a severe restriction on the form of ρ.

It is indeed possible to reduce still further the number of quantities on which the distribution function can depend. Consider again two macroscopic parts of a system, small compared with the whole. We have already seen that two such parts can be considered as quasi-closed, i.e. as practically without mutual interaction, so that they are effectively independent of each other. Let the distribution functions for these two subsystems be ρ_1 and ρ_2, then if we consider the two systems together as a single system, the distribution function ρ_{12} of the latter must, by the multiplication theorem, be equal to the product of the probability densities of its component parts, so that we have

$$\rho_{12} = \rho_1 \rho_2,$$

or

$$\log \rho_{12} = \log \rho_1 + \log \rho_2.$$

Thus the logarithm of the distribution function is an additive quantity, and therefore the logarithm of the distribution function can be a function only of additive integrals of motion, and must itself be an *additive integral of motion*. In other words *the behaviour of the system in a statistical sense is completely determined by the values of the additive integrals of motion.* We know from mechanics that there are seven such integrals, the energy, the three components of momentum, and the three components of angular momentum, and these seven replace the innumerable number of variables which would have to be considered in a mechanical instead of statistical treatment.

Consider a closed system in some given state characterized by given values of all the integrals of motion. The probability density ρ will be zero except at those points of phase space corresponding to these constant values, and at these points $\rho =$ const., by Liouville's theorem. Since, however, the values of the non-additive integrals have no influence on the statistical properties of the system, we can use for ρ the function given by $\rho =$ const. at all points of phase space corresponding to the given constant values of energy, momentum, and angular momentum (they are constant since the system is closed), and $\rho = 0$ for all other points. In other words the probability of finding the closed system in a region of phase space for which the additive integrals have the given values is simply proportional to the volume $d\Gamma$ of the region. This solves the problem of determining the distribution function for a closed system.†

The momentum and angular momentum are associated with the motion—either progressive or rotational—of the body as a whole. Consequently the fact that the statistical properties of the body are determined by the additive integrals alone can be formulated in the following way: *the statistical state of a body in given external conditions undergoing a given motion depends only on its energy.* Thus we see that energy assumes a very special role in statistics. In order to exclude the momentum and angular momentum from the discussion, we shall in future always consider the body in a system of coordinates relative to which it is at rest as a whole.

If the body is not in a state of equilibrium, then the description of its state by the external conditions, its energy, and its motion as a whole is not sufficient; we can, however, adopt the following

† A distribution of this kind is called microcanonical.

procedure. We divide the body into sufficiently small macroscopic parts, which we can consider as in equilibrium; by the preceding considerations the state of each of these parts is then completely determined by its energy, disposition, and motion as a whole. This kind of description of the state of a body, by means of the statistical properties of its subsystems, we can call a *macroscopic* one, in contrast to the mechanical description in which the coordinates and momenta of each particle are given, and which can be called a *microscopic* description.

7. Entropy

We have already pointed out (§ 4) the important fact that all physical quantities characteristic of the system are, for the overwhelmingly greater part of any sufficiently long time, constant and equal to their mean values, this being the more exactly true the longer the time of observation and the more complicated the system. This means that the probability of various values of such a quantity has a very sharp maximum for the mean value. The 'sharpness' or 'breadth' of this maximum is determined by the value of the relative fluctuation, the breadth increasing with the relative fluctuation. The curve of the probability, or more correctly of the probability density, as a function of the value of the given physical quantity, e.g. the energy, has therefore the form shown in Fig. 1, where, however, the breadth of the maximum is greatly exaggerated.

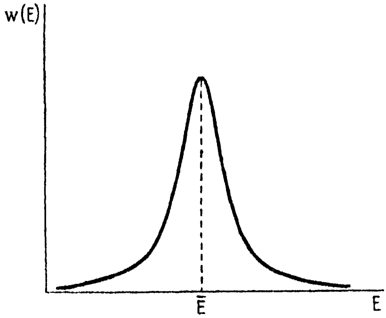


FIG. 1.

In other words any macroscopic system, and in particular any macroscopic part of a closed system, spends nearly all its time in a small region of phase space corresponding to values of physical quantities close to their mean values, and where the distribution function is appreciably different from zero. This region (for the ith subsystem) we denote by $\Delta\Gamma_i$; we shall define it more precisely below.

In § 6 it was shown that for a closed system the probability of

finding the system in a given volume of phase space is proportional to the size of this volume, consequently *the probability of a given macroscopic state of the system is proportional to the quantity* $\Delta\Gamma$, where

$$\Delta\Gamma = \prod_i \Delta\Gamma_i. \tag{7.1}$$

We shall now find a relation between the $\Delta\Gamma_i$ and ρ, the probability density.

Let us write
$$\log\rho = U, \tag{7.2}$$
then, by § 5, U is an additive integral of motion of the given system, and we shall now consider the probability $\rho\,d\Gamma$ or $e^U\,d\Gamma$ as a function of U, that is, we shall introduce the probability of various values of U for the system, denoting this probability by $w(U)\,dU$, where $w(U)$ is a sort of 'probability density' for U. It can evidently be expressed as

$$w(U)\,dU = \rho\,d\Gamma = e^U(d\Gamma/dU)\,dU. \tag{7.3}$$

Here $d\Gamma$ is the volume element of phase space containing those points for which the corresponding U is in the interval dU.

$w(U)$ as a function of U has the same form as the probability function for energy shown in Fig. 1, and has therefore a very sharp maximum for the value of U equal to its mean value $\overline{U}$. Further, $w(U)$ must evidently satisfy the normalization condition:

$$\int w(U)\,dU = 1,$$

which means, in geometrical terms, that the area under the $w(U)$ curve is unity. Consider instead of this curve a rectangle whose height is the maximum value of $w(U)$ (i.e. $w(\overline{U})$, since the maximum is at $U = \overline{U}$) and whose area is unity. The breadth of the rectangle will then be a small quantity ΔU given by

$$w(\overline{U})\Delta U = 1, \tag{7.4}$$

and evidently the interval ΔU around U gives the order of magnitude of the range of values of U for which the probability is appreciably different from zero. Bearing in mind the definition of $w(U)$ (7.3), we can write (7.4) as

$$e^{\overline{U}}\frac{d\Gamma}{dU}\Delta U = e^{\overline{U}}\Delta\Gamma = 1, \tag{7.5}$$

where $\Delta\Gamma$ is the region of phase space corresponding to the interval ΔU of U (in the sense explained above). We shall call the quantity $\Delta\Gamma$, i.e. the 'width' of the statistical distribution, the *statistical*

weight of the state. The statistical weight specifies the size of the region of phase space for which ρ has values appreciably different from zero, and provides in fact the more precise definition of the regions of phase space which we mentioned at the beginning of this section. Thus the quantities $\Delta\Gamma_i$ which were introduced there, are the appropriate statistical weights of the subsystems. We should emphasize that the whole of the above discussion referred to systems forming small parts of some closed system, i.e. to subsystems, and that the suffix i was left out in $\Delta\Gamma$ for reasons of convenience only.

It is usual to call the logarithm of the statistical weight $\Delta\Gamma$ the *entropy* σ of the system,†

$$\sigma = \log \Delta\Gamma, \tag{7.6}$$

and in this form this definition can be applied to any small part of a closed system.

The statistical weight is obviously a multiplicative quantity, i.e. for a system consisting of several component systems it is equal to the product of the statistical weights of the components, and consequently *entropy is an additive quantity.* In particular we can obtain the entropy σ of a closed system as the sum of the entropies σ_i of its components. Thus by (7.6)

$$\sigma = \sum_i \sigma_i = \sum_i \log \Delta\Gamma_i = \log \Delta\Gamma, \tag{7.7}$$

where $\Delta\Gamma$ refers to the phase space of the whole closed system.

From (7.5) and (7.6) it follows that

$$\sigma = \log e^{-U} = -\overline{U},$$

and by the definition of U we can also write for the ith subsystem

$$\sigma_i = \overline{\log (1/\rho_i)}. \tag{7.8}$$

Thus *we can define the entropy of the subsystem as the mean value of the logarithm of the reciprocal of the distribution function.*

Making use of the definition of mean values, this can be put in the form

$$\sigma_i = \int \rho_i \log(1/\rho_i)\, d\Gamma_i, \tag{7.9}$$

where the integration is extended over all the phase space of the given subsystem. The entropy of the whole complex system is thus

$$\sigma = \sum_i \int \rho_i \log(1/\rho_i)\, d\Gamma_i. \tag{7.10}$$

It is necessary to make one important remark about the dimen-

† The idea of entropy was first introduced into physics by Clausius in 1854.

sions of entropy. The statistical weight, like any other volume of phase space, being the product of n elements of momentum and n elements of coordinates (n is the number of degrees of freedom), has obviously the dimensions of the nth power of an action, i.e. [(cm. gm. sec.$^{-1}$)^n]. The entropy has consequently the dimensions of the logarithm of the nth power of an action. This means that for a change of units of action, the entropy changes by an additive constant, for if the unit of action is divided by a, the statistical weight $\Delta\Gamma$ will be multiplied by a^n, and will be in the new units $\Delta\Gamma' = a^n\Delta\Gamma$; the new value of entropy is therefore

$$\sigma' = \log\Delta\Gamma' = n\log a+\log\Delta\Gamma = \sigma+n\log a.$$

For this reason *the value of the entropy can be determined only apart from an additive constant* depending on the choice of units. Differences of entropy for different states, or changes of entropy corresponding to changes of state, are however, quantities independent of the choice of units.

We may note that in quantum mechanics entropy can be defined as a dimensionless quantity, and can therefore be determined without the ambiguity of an additive constant.

8. The law of increasing entropy

The entropy of a closed system was defined as the logarithm of the region $\Delta\Gamma$ of phase space occupied by the system in the macroscopic state concerned, and we have seen that for a closed system $\Delta\Gamma$ is proportional to the probability of this state. Moreover, by definition of statistical equilibrium, the macroscopic state corresponding to this equilibrium is the state of greatest probability. Consequently the quantity $\Delta\Gamma$ and therefore its logarithm have maximum values for statistical equilibrium, which leads at once to the important conclusion that *the entropy of a closed system has its greatest value for the state of statistical equilibrium.*

If we observe a closed macroscopic system in a state for which the entropy has not its maximum value, then after an interval of the order of magnitude of the time of relaxation for equilibrium, the entropy must necessarily reach this maximum value, and there is no reason for it to depart from the maximum again after a further equal interval. These considerations suggest not only that the entropy always tends to reach its maximum value, but its progress to the maximum is a monotonic one, and we shall now show that this is indeed the case.

Consider a closed macroscopic system at time t, and suppose it divided into relatively small parts, each of which has its own distribution function, ρ_i for the ith part, depending on the coordinates and momenta of this part. The entropy σ of the whole system at time t will, by (7.10), be

$$\sigma = \sum_i \int \rho_i \log(1/\rho_i)\, d\Gamma_i = \sum_i \overline{\log(1/\rho_i)} = \overline{\log(1/\prod_i \rho_i)},$$

where the summation is extended over all the parts of the system. Because of the quasi-independence of the parts it is possible, as we saw above, to introduce the distribution function ρ for the whole system equal to the product of all the ρ_i. We then have

$$\sigma = \overline{\log(1/\rho)}.$$

In order to obtain the distribution function at a later time t', the equations of motion of the closed system must be applied and ρ changes to some function ρ'. To obtain the probability at t' for the ith part alone, $\rho'\, d\Gamma_1\, d\Gamma_2 \ldots$ must be integrated over all the phase spaces with the exception of that corresponding to the ith part. If this probability is denoted by $\rho'_i\, d\Gamma_i$, then we shall have for this distribution function:

$$\rho'_i = \int_1 \int_2 \ldots \int_{i-1} \int_{i+1} \ldots \rho'\, d\Gamma_1\, d\Gamma_2 \ldots d\Gamma_{i-1}\, d\Gamma_{i+1} \ldots \tag{8.1}$$

(notice that ρ' is no longer equal to the product of all the ρ'_i†), which describes how the macroscopic state has changed from t to t'. The entropy at t' is

$$\sigma' = \sum \rho'_i \log(1/\rho'_i)\, d\Gamma_i = \sum_i \overline{\log(1/\rho'_i)},$$

where, under the bar, multiplication by $\rho'\, d\Gamma_1\, d\Gamma_2 \ldots$ and integration over all the differentials should be understood.

We now make use of the well-known inequality valid for $x > 0$ that

$$\log x \leqslant x - 1.$$

If we substitute for x the ratio $\left(\prod_i \rho'_i\right)/\rho'$ (we repeat that $\rho' \neq \prod_i \rho'_i$, the ρ_i being defined by (8.1)), we obtain

$$\log\frac{1}{\rho'} - \sum_i \log\frac{1}{\rho'_i} \leqslant \frac{\prod_i \rho'_i}{\rho'} - 1.$$

† The reason for this is that ρ' does not correspond to an arbitrarily chosen state (such as that corresponding to ρ) but has arisen from a state, which as the proof will show, is one of smaller entropy. This will become clearer after the discussion of Fig. 2, p. 22 (ρ' corresponds to a point of type 2, while ρ corresponds to a point of type 3).

Multiplying both sides by $\rho' d\Gamma_1 d\Gamma_2...$ and integrating over all the differentials, the right-hand side gives zero, since

$$\int \prod_i \rho_i' \, d\Gamma_1 \, d\Gamma_2... = \prod_i \int \rho_i' \, d\Gamma_i = 1$$

by the normalization condition, and of course $\int \rho' \, d\Gamma_1 \, d\Gamma_2...$ is also equal to 1.

The left-hand side gives

$$\overline{\log(1/\rho')} - \sum_i \overline{\log(1/\rho_i')},$$

or, since by definition the last term is equal to σ',

$$\overline{\log(1/\rho')} - \sigma' \leqslant 0.$$

Now as can be seen from considerations similar to those of §6 (p. 14), it follows from Liouville's theorem that

$$\overline{\log(1/\rho')} = \overline{\log(1/\rho)},$$

and since $\overline{\log(1/\rho)}$ is the initial entropy σ, we have

$$\sigma' \geqslant \sigma. \tag{8.2}$$

We have in fact proved the *law of increasing entropy* ('the second law of thermodynamics'; the first law being the conservation of energy): *if the state of a closed system is given macroscopically at any instant, then the most probable state at any other instant will be one of greater entropy.*

We shall now examine the significance of this law (which was, incidentally, discovered by Clausius) a little more closely. The equations of mechanics are symmetrical for a replacement of t by $-t$, and so if they admit of some process accompanied by an increase of entropy, they should also admit of the reverse process, the system going through the same configurations in the reverse order, with decrease of entropy. It might seem at first sight that the law of increasing entropy destroys the possibility of such reverse processes, but actually the formulation given above is not in the least contradictory to the symmetry of future and past, since we spoke only of the most probable sequel to a macroscopically described state.

This becomes clearer if we bear in mind that in the above proof no use was made of the fact $t' > t$, and $\sigma' \geqslant \sigma$ is true also for $t' < t$. In other words, the law of increasing entropy means only that if some macroscopically described state (actually the corresponding multitude of microscopic states of the system) is given, then of all the microscopic states satisfying the given macroscopic description an overwhelming majority would give an increase of entropy (or at least

the same entropy) at a later time. At the same time an overwhelming majority of these states have also arisen out of states of greater entropy.

For a further clarification of this symmetry, consider a closed system in statistical equilibrium over such a long interval of time that it will have had an opportunity (very rarely, of course) to carry out some fluctuations, i.e. to go into states for which the entropy has values smaller than the maximum (which it has in equilibrium). It is these fluctuations which reveal the symmetry with respect to both directions in time. Consider a macroscopically described state of the system for which the entropy has less than its maximum value, then of the whole number of cases in which the system comes into this state, the overwhelming majority are cases in which this state represents a maximum deviation from statistical equilibrium. In other words, before the system came into this state the entropy was diminishing, but immediately afterwards it was increasing again, so that the entropy was increasing in both directions of time in accordance with complete symmetry as regards these directions. This is illustrated by plotting σ as a function of t (Fig. 2). What we have just said means that if we observe an entropy σ' different from the maximum entropy σ_{max}, then it is overwhelmingly probable that this state will be represented by a point of type 1 rather than one of type 2. In other words, the probability of a fluctuation for which the entropy decreases still farther than σ' is very much less than one for which the entropy has a minimum. This is connected with the fact that the probability of a state becomes rapidly smaller the larger the deviation of the corresponding entropy from its equilibrium value.

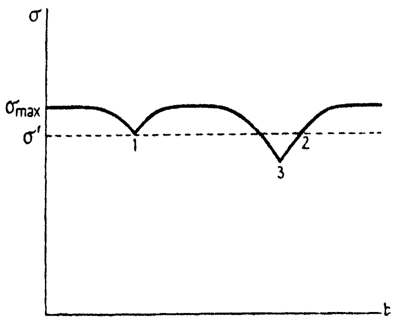


FIG. 2.

If we consider the whole universe as a single closed system obeying the laws of statistics, then it follows that it must be in a state of statistical equilibrium, this being the overwhelmingly most probable state for a closed system. In other words, the history of the universe should be invariant for the transformation from future to past, which would mean that together with each physical process (in

particular, processes causing increase of entropy) there must also take place the reverse process (in particular processes which diminish the entropy of the whole universe). In reality, observation shows that our own part of the universe is certainly not in statistical equilibrium, and everyday experience shows that both directions of time are certainly not equivalent, so that the behaviour of the universe contradicts the requirement of statistics that it should nearly always be in a state of equilibrium symmetrical with respect to future and past.

Boltzmann attempted to remove this contradiction by his 'fluctuation hypothesis'. He suggested that in the relatively small part of the universe observed by us, chance fluctuations from the statistical equilibrium of the whole universe are taking place, or, in other words, the impression that the universe does not obey statistical laws is due to our part of the universe being in the course of an enormous fluctuation. The fact that it is possible to observe such a colossal fluctuation (over a volume exceeding 10^{75} c.c.) Boltzmann explained by supposing that just such a fluctuation is a necessary condition for the existence of the observer (a condition favouring biological development of organisms, for instance). This argument is, however, quite false, since there would be an enormously greater probability of a smaller fluctuation for which there existed for instance only a single observer, without the myriads of stars prepared for him, and in any case it would be sufficient for the possibility of observing the universe to have this deviation from equilibrium in a volume of only 10^{55} c.c. (containing the sun and nearest stars). In this connexion we should remark that the probability of fluctuations is so small that it is in general not possible to observe any appreciable fluctuations at all.

This contradiction between the actual behaviour of the universe and the requirements of statistics, like every other contradiction between theory and reliable experiments, arises from the fact that the theory is not quite applicable to the experiment in question. In the present case it indicates that processes must exist in the universe to which the mechanics of which statistics is a consequence cannot be applied. It is only a closed system obeying statistical laws which has to be in a state of statistical equilibrium. In fact that part of the universe which obeys statistics is not a closed system, while the universe as a whole is a closed system but does not obey the laws of statistics.

If a system is closed during a time small compared with the relaxation time for establishing equilibrium, then we can no longer say that its entropy has a maximum value and the law of increasing entropy becomes the law of monotonic change of entropy, that *during this time the entropy changes monotonically* (strictly speaking, a monotonic change is overwhelmingly probable).†

We can deduce a most important result from these considerations. If a system is isolated from the external world for a time short compared with the relaxation time, then, as we have said, its entropy must change monotonically. The same is true of a second isolated (closed) system and it can be shown that the time direction for which the entropy of one system increases is the same as that for the other; this follows if we consider the two systems concerned as a single system. If the law of monotonic change is applied to the compound system it is easy to see that the time directions for entropy increase of the two parts cannot be opposite, for if the reverse were true the two systems could be connected so that the sum of their entropies did not change monotonically.

Thus the two directions of time are not equivalent, and that direction for which the entropy of any temporarily closed macroscopic system increases is called the *future*, while the opposite direction is the *past*. This is in fact the physical definition of future and past, while the definition arising from the concepts 'it has not yet happened' and 'it has already happened' is one based on the properties of human psychology. Having made this definition we can now express the law of monotonic change of entropy as one of monotonic *increase*, and we formulate it by saying that the entropy of a closed system does not decrease with time (it either increases or remains constant). As regards the possibility of decreasing entropy by means of fluctuations, it has such small probability as to have no practical significance.

The concepts of future and past are completely foreign to classical mechanics, where there is absolutely nothing to distinguish the two directions of time from each other. They are foreign also to statistics if we apply it only to closed systems, but they arise in practice because that part of the universe to which the theory has to be applied is not always a closed system.

† This result is stated here without proof, since we have not succeeded in showing clearly how it is connected with the previous considerations.

Since we can observe only such processes for which the entropy of a closed system increases, or in the limiting case remains constant, it is usual to divide all processes taking place in closed systems into *irreversible* and *reversible* processes, corresponding to these two possibilities. The former are accompanied by increase of entropy, and evidently we cannot observe processes in nature which take place in the reverse order, since they would be accompanied by a decrease of entropy; hence their name. On the other hand, a reversible process, since it is accompanied by no change of entropy, can equally well take place in the reverse direction. We should point out that the entropies of the individual parts of a system need not be constant in a reversible process.

III

THE THERMODYNAMIC FUNCTIONS

9. Temperature

THE considerations of the previous chapter have shown that macroscopic systems behave in accordance with laws of a special kind—the laws of statistics, and precisely because of these laws there are a number of quantities which characterize a macroscopic body but have no meaning for the individual particles (such as molecules) of the body. A quantity of this kind is for instance the entropy, introduced in § 7, and there are a number of others which we shall discuss in this chapter: they are called *thermodynamic* functions or quantities, and we shall deduce a number of relations between them known as *thermodynamic relations* which are true independently of the particular system to which they may refer. We may remark that since the law of increasing entropy has a much wider field of application than classical statistics (based on classical mechanics), the thermodynamic relations which are a consequence of this law also have a much more general application than the concrete results of classical statistics.

Consider again a closed macroscopic system, which by a suitable choice of coordinates can be regarded as at rest, and suppose that the system is in a state of statistical equilibrium, that is to say (§ 8) that its entropy has the maximum value consistent with the given energy of the system (this maximum value being a function of the energy).

Suppose now that this system consists of two bodies in equilibrium with each other. If the energies of these bodies are E_1 and E_2, then the total energy of the system is

$$E = E_1+E_2,$$

since the interaction of the macroscopic bodies can be neglected in comparison with their internal energies (§ 6). The entropy σ of the whole system is, as we know, an additive quantity and therefore equal to the sum of the separate entropies:

$$\sigma = \sigma_1(E_1)+\sigma_2(E_2).$$

The necessary condition for a maximum entropy is

$$d\sigma = \frac{d\sigma_1}{dE_1}dE_1+\frac{d\sigma_2}{dE_2}dE_2 = 0. \qquad (9.1)$$

The total energy E remains constant since the system is closed, or

$$dE = dE_1 + dE_2 = 0.$$

So (9.1) becomes
$$\left(\frac{d\sigma_1}{dE_1} - \frac{d\sigma_2}{dE_2}\right) dE_1 = 0,$$
or
$$d\sigma_1/dE_1 = d\sigma_2/dE_2.$$

This analysis applies also for the case of any number of bodies in equilibrium with each other, as can be seen by applying the result to any pair of such bodies. Each such pair is not of course a closed system in itself, but in order that the entropy should have its maximum value for all the bodies together it must in particular be a maximum for processes for which the energy of the given pair remains constant, i.e. the condition (9.1) is still necessary. Thus if the system is in statistical equilibrium, the derivative of the entropy with respect to the energy is the same for all parts of the system, i.e. constant throughout the system. The reciprocal of this differential coefficient is known as the *temperature*, θ, of the system,

$$\frac{d\sigma}{dE} = \frac{1}{\theta}. \tag{9.2}$$

Consequently *the temperatures of bodies in equilibrium with each other are equal*:
$$\theta_1 = \theta_2 = \dots.$$

It will be seen that temperature is a purely statistical quantity and only has a meaning with reference to macroscopic bodies. It should also be noticed that entropy, energy, and temperature are functions of each other as follows from their definitions, and so any one of them will in general serve to determine the other two.

Suppose next that we have two interacting bodies each of which is in some state of equilibrium, but which are not in equilibrium with each other, and, further, that the two bodies together form a closed system. Their temperatures θ_1 and θ_2 are given by

$$\frac{d\sigma_1}{dE_1} = \frac{1}{\theta_1}, \qquad \frac{d\sigma_2}{dE_2} = \frac{1}{\theta_2}.$$

In the course of time equilibrium will be established between the two bodies, while their temperatures gradually become equal. Their total entropy, which is equal to the sum of their separate entropies ($\sigma = \sigma_1 + \sigma_2$), must increase during this process (§ 8), i.e.

$$d\sigma = d\sigma_1 + d\sigma_2 = \frac{dE_1}{\theta_1} + \frac{dE_2}{\theta_2} > 0.$$

Since their total energy E_1+E_2 is conserved, we have as before $dE_2 = -dE_1$, and so

$$dE_1\left(\frac{1}{\theta_1}-\frac{1}{\theta_2}\right) > 0. \tag{9.3}$$

Let the temperature of the second body be higher than that of the first, i.e. $\theta_2 > \theta_1$, then

$$\left(\frac{1}{\theta_1}-\frac{1}{\theta_2}\right) > 0,$$

and so from (9.3) we obtain

$$dE_1 > 0.$$

In other words, the energy of the second body diminishes by dE_1 while the energy of the first is increased by the same amount. We have in fact shown that *energy will go over from a body at a higher temperature to one at a lower temperature.*

As follows from its definition, temperature has the dimensions of an energy, and can therefore be measured in energy units, such as ergs for instance. In practice, however, it is usual to measure temperature in special units called degrees. If θ denotes the temperature measured in ergs and T the same temperature measured in degrees, than we have the relation

$$\theta = kT, \tag{9.4}$$

where the coefficient of proportionality k, i.e. the number of ergs per degree, is known as Boltzmann's constant and has the value

$$k = 1{\cdot}372.10^{-16} \text{ ergs/degree.}$$

Similarly, it is usual to employ, instead of σ, a quantity S, also called entropy, and defined as

$$S = k\sigma. \tag{9.5}$$

The definition of temperature (9.2) can then be written as

$$\frac{dS}{dE} = \frac{1}{T}. \tag{9.6}$$

In the rest of the book we shall sometimes use σ and θ, and sometimes S and T to denote entropy and temperature, according to which is the more convenient.

10. Macroscopic motion

If a closed system is in uniform progressive or rotational motion, we can always find a system of coordinates with respect to which the system is at rest as a whole. We shall now show that if the system is in statistical equilibrium this coordinate system will also

be the one with respect to which all the parts of the closed system are at rest. In other words, we shall show that *there is no macroscopic motion of the individual parts of a closed system in statistical equilibrium.*

Consider some part of the closed system (i.e. a subsystem) and suppose it is moving as a whole with velocity v relative to the closed system. Let $\sigma(E)$ be the entropy of the subsystem in the coordinate system with respect to which the subsystem is at rest, where E is the energy of the subsystem in this frame of reference, i.e. the internal energy of the subsystem. Evidently $E = E_{\text{tot}} - E_{\text{kin}}$, where E_{tot} is the total energy of the subsystem and E_{kin} its kinetic energy of motion as a whole; thus $\sigma = \sigma(E_{\text{tot}} - E_{\text{kin}})$. We shall suppose that the states of all the remaining parts of the closed system are given; then since the energy of the whole closed system is constant, this must also be true of the total energy of the given subsystem.

The conditions for maximum entropy of the closed system in equilibrium now become the conditions of maximum entropy of the given subsystem. One of these conditions is

$$\partial\sigma/\partial p = 0, \tag{10.1}$$

where p is the total momentum of the given subsystem. Now

$$\frac{\partial\sigma}{\partial p} = \frac{\partial\sigma}{\partial E_{\text{kin}}}\frac{\partial E_{\text{kin}}}{\partial p} = -\frac{v}{\theta} = -\frac{p}{M\theta}, \tag{10.2}$$

since $\partial\sigma/\partial E_{\text{kin}} = -\partial\sigma/\partial E = -1/\theta$, where θ is the temperature of the system; $\partial E_{\text{kin}}/\partial p = -v$ is the velocity of the given subsystem, and M its mass. Thus the condition (10.1) gives $v = 0$, which proves the proposition stated above.

In order that σ as a function of p should have a maximum and not a minimum, it is necessary that in addition to (10.1) we should also have $\partial^2\sigma/\partial p^2 < 0$. Using (10.2) this gives

$$\frac{\partial^2\sigma}{\partial p^2} = -\frac{1}{M\theta} + \frac{p}{M\theta^2}\frac{\partial\theta}{\partial p} < 0,$$

and since $p = 0$, we obtain $\qquad \theta > 0. \qquad$ (10.3)

Thus *the temperature is always positive.*

11. Adiabatic processes

If a body is subject to no interactions, except changes of the external conditions in which it is placed (for instance it may be in a variable external field), then it is said to be thermally isolated.

A thermally isolated body is not of course in general a closed system, and its energy may change with time.

We may remark that since a thermally isolated system differs from a closed one only in that its Hamiltonian function may vary with time, the law of increasing entropy will still hold for it, for in the deduction of this law we made no use of the independence of $E(p, q)$ of time.

A specially important case is when the external conditions in which the body is placed vary only very slowly. A process of this kind taking place in a thermally isolated body is said to be *adiabatic*. We shall now show that *the entropy remains constant in an adiabatic process, i.e. that such a process is reversible.*

The external conditions can be characterized by 'external' parameters, and we shall assume (for brevity of treatment) that there is only one such parameter λ. The time derivative of entropy, dS/dt, will depend on the rate of change $d\lambda/dt$ of the parameter. Since $d\lambda/dt$ is small, dS/dt can be expanded in powers of $d\lambda/dt$. Obviously there is no term of zero order (i.e. not containing $d\lambda/dt$), since if $d\lambda/dt = 0$, dS/dt also vanishes. The term in $d\lambda/dt$ is also absent, since such a term would change sign with change of sign of $d\lambda/dt$, while dS/dt must always be positive in accordance with the law of increasing entropy. Thus the expansion begins only with the second power of $d\lambda/dt$, or, neglecting higher order terms,

$$(dS/dt) = A(d\lambda/dt)^2,$$

and hence

$$dS/d\lambda = A\, d\lambda/dt.$$

It follows that as $d\lambda/dt$ approaches zero so also does $dS/d\lambda$, and this proves the reversibility of an adiabatic process.

We shall now determine the change of energy of a body which undergoes an adiabatic process. By definition the energy E is

$$E = \overline{E(p, q, \lambda)}$$

(the mean being taken over p and q, but not over λ), where $E(p, q, \lambda)$ is the energy as a function of the coordinates and momenta of the given system, and in addition of the external parameters. Since the operations of averaging and differentiation with respect to time can be carried out in any order without affecting the result, we have

$$\frac{dE}{dt} = \frac{d\overline{E(p, q, \lambda)}}{dt} = \overline{\frac{dE(p, q, \lambda)}{dt}} = \overline{\frac{\partial E(p, q, \lambda)}{\partial \lambda}\frac{d\lambda}{dt} + \frac{\partial E}{\partial p}\frac{dp}{dt} + \frac{\partial E}{\partial q}\frac{dq}{dt}}$$

($d\lambda/dt$ is independent of p and q, and can therefore be taken outside the averaging bar).

Now by Hamilton's equations

$$\dot{q} = \partial E/\partial p, \qquad \dot{p} = -\partial E/\partial q.$$

So we have the identity

$$\frac{\partial E}{\partial p}\frac{dp}{dt}+\frac{\partial E}{\partial q}\frac{dq}{dt} = 0,$$

and we are left with

$$\frac{dE}{dt} = \overline{\frac{\partial E(p,q,\lambda)}{\partial \lambda}}\frac{d\lambda}{dt}. \tag{11.1}$$

Since the process takes place at constant entropy, and the energy E can be regarded as a function of σ and λ, dE/dt can be written as

$$\frac{dE}{dt} = \left(\frac{\partial E}{\partial \lambda}\right)_\sigma \frac{d\lambda}{dt}, \tag{11.2}$$

where the suffix σ means that differentiation is taken at constant entropy.

Comparing (11.1) and (11.2), we have

$$\left(\frac{\partial E}{\partial \lambda}\right)_\sigma = \overline{\frac{\partial E(p,q,\lambda)}{\partial \lambda}}.$$

In the case of several external parameters $\lambda_1, \lambda_2, \ldots$ this relation holds for each one of them separately, and we denote the differential coefficient of the energy with respect to the ith parameter by $-\Lambda_i$, i.e.

$$\overline{\frac{\partial E(p,q,\lambda_1,\lambda_2,\ldots)}{\partial \lambda_i}} = \left(\frac{\partial E}{\partial \lambda_i}\right)_\sigma = -\Lambda_i. \tag{11.3}$$

This formula allows the calculation of a whole number of mean values in a purely thermodynamic way.

12. Pressure

If a body is in statistical equilibrium, its entropy (for a given energy) and its energy for given entropy depend only on the volume and not on the shape of the body. A change of shape of the body can in fact be regarded as a mere transposition of the various parts of the body, which cannot change the entropy and energy if the body is in no external field, because these are additive quantities and therefore equal to the sum of the entropies and energies of the separate parts.

Thus the macroscopic state of a body in equilibrium (and in no external field) is completely determined by only two quantities,

for instance its energy and volume, and all other physical quantities characteristic of the body in this state are functions of these two quantities (we can of course use any other pair of thermodynamic quantities instead of energy and volume).

We shall now determine the average force exerted by the body on the boundary which limits its volume. The force in any direction is the component in that direction of the gradient of the energy, taken with a negative sign, and therefore the force acting on an element of area **dS** may be written as

$$\mathbf{F} = -\partial E(p, q, \mathbf{r})/\partial \mathbf{r},$$

where $E(p, q, \mathbf{r})$ is the energy of the body as a function of the coordinates and momenta, and $\mathbf{r}$ is the vector distance of the element of area from some origin (the differential coefficient with respect to the vector $\mathbf{r}$ means a vector whose components are equal to the differential coefficients with respect to the corresponding components of $\mathbf{r}$, i.e. the gradient).

Averaging both sides of the above equation, we have by (11.3)

$$\overline{\mathbf{F}} = -\frac{\overline{\partial E(p, q, \mathbf{r})}}{\partial \mathbf{r}} = -\left(\frac{\partial E}{\partial \mathbf{r}}\right)_S = -\left(\frac{\partial E}{\partial V}\right)_S \frac{\partial V}{\partial \mathbf{r}},$$

V being the volume. Now the element of volume is $\mathbf{dSdr}$, so

$$\partial V/\partial \mathbf{r} = \mathbf{dS},$$

and

$$\overline{\mathbf{F}} = -\left(\frac{\partial E}{\partial V}\right)_S \mathbf{dS}.$$

We see, therefore, that the mean force on an element of area is directed along the normal to the surface and proportional to the area of the element (Pascal's law). The absolute value of this force per unit area of the surface is

$$p = -(\partial E/\partial V)_S. \tag{12.1}$$

This quantity is known as the *pressure.*

The relations

$$T = (\partial E/\partial S)_V, \qquad p = -(\partial E/\partial V)_S \tag{12.2}$$

may be written in the form of an equation between complete differentials; thus

$$dE = T\,dS - p\,dV. \tag{12.3}$$

This equation is very important and we shall call it the *thermodynamic identity.*

One of the most important properties of pressure is that *the*

pressures of bodies in equilibrium with each other (or the pressures of different parts of a uniform system) are equal. This follows immediately from the fact that in equilibrium the forces which any two such bodies exert on each other (across their surfaces of contact) must balance each other, so that the absolute values of these forces (proportional to the pressures) must be equal.

The equality of pressure of bodies in equilibrium can also be deduced from the condition of maximum entropy, in the same way as equality of temperature was deduced in § 9. Consider any two parts of a closed system in equilibrium, then in order that the entropy of the whole system should be a maximum, it must in particular be a maximum as regards processes which change the volumes of only these two parts. The sum of the two volumes must remain constant in such a process, since the volume of the whole closed system is constant. Let S_1 and S_2 be the entropies of these two parts, then the necessary condition for a maximum is

$$\frac{\partial S_1}{\partial V_1} dV_1 + \frac{\partial S_2}{\partial V_2} dV_2 = 0,$$

or since $dV_1 = -dV_2$, $\quad \partial S_1/\partial V_1 = \partial S_2/\partial V_2.$

But from (12.3), which can be written as

$$dS = dE/T + p\,dV/T,$$

it follows that $\partial S/\partial V = p/T$, and so we obtain

$$p_1/T_1 = p_2/T_2.$$

Since the temperatures of both parts are equal in equilibrium, it follows that the pressures must also be equal, i.e.

$$p_1 = p_2.$$

When equilibrium is established the equality of pressures is achieved much more rapidly than equality of temperatures, so that we often have the case of a system with the same pressure, but not the same temperature throughout. The reason for this is that inequality of pressure is associated with mechanical forces which cause macroscopic motion, thus bringing about equalization of pressure more rapidly than equalization of temperature, the latter not being associated with macroscopic motion.

If the body is not in the state of equilibrium corresponding to given energy and volume, its state is determined not only by the

energy and volume but by certain additional parameters, which we shall denote by ξ_i. The thermodynamic identity in this case becomes

$$dE = T\,dS - p\,dV + \sum_i \Xi_i \xi_i, \tag{12.4}$$

where the Ξ_i are functions of the state.

13. Work and quantity of heat. Specific heats

In the course of processes taking place in a body, it may receive or lose energy in two ways. If the body is thermally isolated, then the increase of its energy due to change of the external conditions is called the *work done on the body* (the same quantity taken with the opposite sign is called the *work done by the body*). In the general case, however, a body which is not thermally isolated may also receive energy from (or lose energy to) other bodies directly, which is not associated with a change of external conditions. This part of the energy change of the body is called the *heat received or given up by the body*. Thus the change of energy dE in any process is made up of the work dW done on the body and the quantity of heat dQ received by it:

$$dE = dW + dQ. \tag{13.1}$$

A very important example of work is that connected with a change of volume of the body (a change of volume can of course be regarded as a change of external conditions). Let us suppose that the process takes place so slowly that the body can at each moment be considered as in the statistical equilibrium corresponding to the appropriate volume at that moment, and to the given energy; then, as we have seen,

$$dE = T\,dS - p\,dV.$$

In order to identify dW and dQ in this equation we shall assume that the body is thermally isolated, so that since the process takes place very slowly (therefore adiabatically), $S =$ const. and $dS = 0$. Thus the work done on the body is

$$dW = -p\,dV, \tag{13.2}$$

and consequently the quantity of heat received by the body in the general case (i.e. when it is not thermally isolated) is

$$dQ = T\,dS. \tag{13.3}$$

The quantity of heat dQ and the work dW are not perfect differentials of suitable quantities Q and W (in fact the notation dQ, dW is not quite appropriate); it is only the sum $dQ + dW = dE$ which is a perfect differential, and although it is permissible to speak

of the energy E in any given state, we cannot for instance speak of the quantity of heat possessed by the body in this state. In other words the energy of a body cannot be divided into a thermal and a mechanical part, except when we are dealing with *changes* of energy. The change of energy when the body goes from one state to another can indeed be divided into the quantity of heat received (or given up) by it and the work done on it (or by it), but this division is not uniquely determined by the initial and final states, and depends on the nature of the transition process. In fact, *the quantity of heat and the work are functions of the process taking place in the body and not functions of its state.* This is particularly clearly illustrated in the case of a *cyclic* process, i.e. one which commences and finishes in the same state. The change of energy for such a process is always zero, while at the same time the body can receive (or give out) a quantity of heat (or work). Mathematically this is expressed by the fact that the integral round the cycle of the perfect differential dE is equal to zero, while that of dQ or dW is not zero, because these are not perfect differentials.

The quantity of heat which when received by a body raises its temperature by one unit (for instance, one degree) is called the *heat capacity* or *specific heat* of the body.† It will be seen that the specific heat depends on the conditions in which the rise of temperature takes place. Thus we may distinguish between the specific heat at constant volume (C_v) and that at constant pressure (C_p), and evidently

$$C_v = T(\partial S/\partial T)_v, \tag{13.4}$$

$$C_p = T(\partial S/\partial T)_p. \tag{13.5}$$

If a body is not in the state of equilibrium and irreversible processes are taking place, then, writing (12.4) in the form

$$T\frac{dS}{dt} = \frac{dE}{dt} + p\frac{dV}{dt} - \sum_i \Xi_i \frac{d\xi_i}{dt}, \tag{13.6}$$

we can say that the change of the ξ_i with time must be such as to increase S (in accordance with the law of increasing entropy), or in other words $-\sum_i \Xi_i d\xi_i/dt \geqslant 0$. Hence for an irreversible process

$$T\frac{dS}{dt} \geqslant \frac{dE}{dt} + p\frac{dV}{dt} \tag{13.7}$$

(the equality sign holding in the limiting case of a reversible process).

† Strictly speaking the specific heat is per unit quantity of the body (e.g. per gm. molecule, per gm., per c.c., or per molecule), but we shall use specific heat and heat capacity interchangeably, except where there is any danger of confusion.

Since the equation

$$dQ = dE - dW = dE + p\,dV \tag{13.8}$$

holds also for irreversible processes, we also have

$$\frac{dQ}{dt} \leqslant T\frac{dS}{dt}. \tag{13.9}$$

14. The maximum work

Every form of work can be spent in setting bodies into macroscopic motion. Since, as we have already seen, states in which bodies are in relative motion are not equilibrium states, we have the important result that *no work can be carried out in a closed system in statistical equilibrium.*

As we have already pointed out, the work is a function of the process, and so for a process of transition from one state to another the work done depends on the way the process is carried out, and, in particular, on what other bodies take part, and in which way they take part. We may therefore ask what is the *maximum work* that can be obtained in a transition from a given state to the state of equilibrium. This work taken with the opposite sign, will then be the minimum work required to make the system carry out the reverse process.

If the system concerned is thermally isolated, it is easy to show that the maximum work that it can do in a transition from one state to another is obtained when the transition takes place reversibly. Let the energy of the system in the given state be E_0 and the energy in the state of equilibrium $E(S)$ (the latter being a function of the entropy in the equilibrium state). The entropy S and also the energy E may have different values according to how the transition to equilibrium took place. The total amount of work done by the system, i.e. the kinetic energy, is then $W = E_0 - E(S)$. Differentiating W with respect to S, the final entropy, we obtain $dW/dS = -T$, and since the temperature T is always positive we see that W diminishes with increase of S. Consequently *the maximum work that the system can do is obtained if the entropy of the system remains constant, i.e. if the process is reversible.* In the same way this amount of work taken with the opposite sign is evidently *the minimum work* which must be done by some source of work for the system to carry out the reverse process.

We shall now determine the maximum work that can be done (on some object) in an interchange of a very small amount of heat between two bodies at temperatures T_1 and T_2 (these temperatures remaining constant during the process). Assuming $T_1 > T_2$, suppose the first body loses energy $-dE_1 = -T_1\,dS_1$ and the second receives energy $dE_2 = T_2\,dS_2$. In order that the maximum work should be done this process must be carried out reversibly, i.e. the sum of the entropies of the two bodies must remain constant:

$$dS_1 = -dS_2.$$

The work is then equal to the diminution of the sum of the total energies of the two bodies, i.e.

$$dW_{\max} = -dE_1 - dE_2 = -T_1\,dS_1 - T_2\,dS_2 = -(T_1 - T_2)\,dS_1. \quad (14.1)$$

The ratio of the work done by the system to the maximum work which can be obtained in the given conditions is called the *coefficient of utility*. Alternatively a quantity called the *efficiency* is sometimes used, defined as the ratio of the work done to the quantity of heat taken in by the system. The maximum efficiency for transfer of energy from a body at higher temperature to one at lower temperature is by (14.1) equal to $(T_1 - T_2)/T_1$, since the hotter body loses an amount of energy $-T_1\,dS_1$. It will be noticed that the efficiency differs from the coefficient of utility by just this factor, the maximum value of the efficiency.

In order that a reversible transfer of energy of this kind can take place, it is necessary that the whole system should be in equilibrium throughout the process, or in other words that the bodies between which the energy exchange actually takes place should be at the same temperature. This can be achieved with the help of an auxiliary body which undergoes a so-called *Carnot cycle*. This cycle consists of the auxiliary body receiving energy from the first body at a constant temperature T_1, then being adiabatically cooled to T_2, losing energy at T_2 to the second body, and finally returning adiabatically to its original state. During the expansions associated with these processes the auxiliary body does work on external objects. It should be noticed that if the transfer of energy were to take place *directly* between the hot and cold bodies (at constant volume) no work would be done at all, and the entropy of the two bodies would be increased by $dE(1/T_2 - 1/T_1)$, if dE was the amount of energy transferred.

15. The heat function

If a process is carried out at constant volume, it follows from (13.8) that

$$dQ = dE.$$

If, on the other hand, the pressure is constant, we have

$$dQ = d(E+pV) = dH, \tag{15.1}$$

so that dQ is the differential of a new function H, known as the *heat function*† of the body, and defined as

$$H = E+pV. \tag{15.2}$$

For the differential dH we can write

$$dH = dE + p\,dV + V\,dp,$$

and substituting (12.3) this becomes

$$dH = T\,dS + V\,dp, \tag{15.3}$$

from which we deduce

$$T = (\partial H/\partial S)_p, \qquad V = (\partial H/\partial p)_S. \tag{15.4}$$

If the body is thermally isolated from its surroundings (which, as we have already pointed out, does not mean that the system is closed), then the transfer of heat dQ is zero, and so from (15.1) it follows that at constant pressure

$$H = \text{const}. \tag{15.5}$$

Using the thermodynamic identity (12.3), the specific heat at constant volume (13.4) becomes

$$C_v = (\partial E/\partial T)_v. \tag{15.6}$$

Similarly at constant pressure (13.5) and (15.3) give

$$C_p = (\partial H/\partial T)_p. \tag{15.7}$$

Thus we see that at constant pressure the heat function plays a role similar to that of the energy at constant volume.

16. Stationary flow

We shall now discuss processes of *stationary flow* in which a gas or a liquid flows from one region of constant external conditions to another. The condition for the flow to be stationary is that the pressure at every point of the closed region in which the flow takes place should remain constant (in time) throughout the process. For example, if a gas flows into a vessel through a hole in another vessel,

† This function is also known by a number of other names, such as 'enthalpy', 'total heat', and 'heat content'.

this condition will *not* be fulfilled, since the pressures in the two vessels will change continuously until they equalize. On the other hand, the flow can be made stationary if the transfer of gas from one vessel to the other takes place so slowly that the pressures in the vessels can be considered as constant, or at least varying only very slowly (as for instance if the hole between the vessels is sufficiently small). Another example of a process of stationary flow is that of a gas or liquid along a tube in which the pressure at any point remains constant.

We shall suppose not only that the flow is stationary, but also that it takes place in thermal isolation. The process may, however, be either reversible or irreversible, since the assumption of thermal isolation does not at all imply that the entropy of the system is constant (the quantity of heat dQ in irreversible processes not being equal to $T\,dS$, as was explained in § 13).

Suppose then, that a quantity of gas (or liquid) originally occupying volume V_1 at pressure p_1 goes over (without exchange of heat) into a volume V_2 at pressure p_2, and that during the transition process the pressures p_1 and p_2 remain constant; let the total energy before the transition be $E_{1\,\mathrm{tot}}$, and after the transition $E_{2\,\mathrm{tot}}$. The change of energy $E_{2\,\mathrm{tot}}-E_{1\,\mathrm{tot}}$ is evidently equal to the work done on the gas in reducing the volume by V_1 at pressure p_1, less the work done by the gas itself in occupying volume V_2 at pressure p_2, so

$$E_{2\,\mathrm{tot}}-E_{1\,\mathrm{tot}} = p_1 V_1 - p_2 V_2$$

or

$$E_{1\,\mathrm{tot}}+p_1 V_1 = E_{2\,\mathrm{tot}}+p_2 V_2. \tag{16.1}$$

We can call the quantity $E_{\mathrm{tot}}+pV$ the 'total heat function' in distinction to the heat function $H = E+pV$, since E is the energy not counting the kinetic energy of macroscopic motion, and so we have the result that *for a thermally isolated stationary process*

$$H_{\mathrm{tot}} = E_{\mathrm{tot}}+pV = \text{constant}, \tag{16.2}$$

or in other words *the total heat function is conserved.* If v is the velocity of the system as a whole and M its mass, then (16.2) can be expressed in the form

$$H+\tfrac{1}{2}Mv^2 = E+\tfrac{1}{2}Mv^2+pV = \text{constant}. \tag{16.3}$$

In particular if $v = 0$, i.e. if the system has no macroscopic motion during the process, then (16.3) reduces to conservation of the heat function:

$$H = E+pV = \text{constant}. \tag{16.4}$$

Processes of this kind are known as *Joule-Thomson processes.* During transition from its initial to its final position, a body undergoing a process of this sort must be in strong frictional contact with some other body, in order to have negligible velocity. In the example mentioned at the beginning of this section, this other body would be the wall with a very small hole between the two vessels.

Another special case is the process of stationary reversible flow, and together with the condition of thermal isolation the reversibility means that the process is adiabatic, i.e. that the entropy of the body remains constant. A necessary condition for the possibility of such a process taking place is the *absence* of any friction between the bodies taking part, in distinction to the case of a Joule-Thomson process. This is because friction causes an equalization of the velocities of the rubbing bodies and so causes an approach to equilibrium, which always implies irreversibility of the process.

An example of a reversible stationary process is thermally isolated stationary flow of a fluid along a tube, if friction against the walls can be neglected. In this case the general condition (16.3) can be somewhat changed; if the suffixes 1 and 2 denote values at any two points in the tube for some given mass M of liquid, then (16.3) can be written as

$$H_2-H_1 = \tfrac{1}{2}Mv_1^2-\tfrac{1}{2}Mv_2^2.$$

But since the entropy is a constant for this flow, (15.3) becomes

$$dH = V\,dp,$$

and so the change of heat function is

$$H_2-H_1 = \int\limits_{p_1}^{p_2} V\,dp,$$

where p_1 and p_2 are the pressures at the given points of the tube (we assume there is no external field of force). On account of the small compressibility of a liquid its volume can be assumed constant throughout the flow, and we obtain

$$H_2-H_1 = V(p_2-p_1) = \tfrac{1}{2}Mv_1^2-\tfrac{1}{2}Mv_2^2,$$

or

$$\tfrac{1}{2}Mv_1^2+Vp_1 = \tfrac{1}{2}Mv_2^2+Vp_2,$$

or in other words the quantity

$$\tfrac{1}{2}Mv^2+pV = \text{constant} \tag{16.5}$$

for thermally isolated flow of a liquid.

Dividing this equation by M and remembering that M/V is the density ρ of the liquid, we obtain *Bernoulli's equation*

$$\tfrac{1}{2}v^2+p/\rho = \text{constant}. \tag{16.6}$$

EXAMPLE

Find the speed of flow of an incompressible liquid through a small hole (area s_2) in a vessel, the surface area of the liquid in the vessel being s_1 (the vessel is in the gravitational field).

SOLUTION. If the system is in an external field of force, then the total energy contains also the potential energy of the system in this field. This potential energy must therefore be added to the equations (16.3) and (16.5) which describe the flow of the liquid. If the volume V of the liquid (of mass M) is so small that we can assume all its molecules to be at approximately the same height z above the earth's surface, then (16.5) becomes

$$\tfrac{1}{2}Mv^2+pV+Mgz = \text{constant},$$

and dividing by M we obtain Bernoulli's equation in the form

$$\tfrac{1}{2}v^2+p/\rho+gz = \text{constant}.$$

In our particular case this equation means that the quantity on the right-hand side must be the same for all sections of the vessel. Since the decrease of volume of liquid in the vessel is equal to the volume flowing out,

$$v_1 s_1 = v_2 s_2,$$

where v_1 and v_2 are the velocities of fall of the liquid in the vessel, and of flow through the hole, respectively. Let h be the height of the surface of the liquid above the hole, then if we choose the hole as the origin of z, we have at the surface of the liquid $v = v_1$, $z = h$, and $p = p_0$, the external pressure (e.g. atmospheric pressure), while at the hole $v = v_2$, $z = 0$, and again $p = p_0$.

Thus Bernoulli's equation gives

$$p_0/\rho+gh+\tfrac{1}{2}v_1^2 = p_0/\rho+\tfrac{1}{2}v_2^2,$$

and we find

$$v_2 = \sqrt{\{2gh/(1-s_2^2/s_1^2)\}}.$$

17. The Helmholtz and Gibbs free energies

In § 13 we discussed the work done on (or by) a thermally isolated system; during the process in which the work is done, the temperature will of course change. Suppose now that the system is not thermally isolated but is kept instead at constant temperature; to accomplish this it will evidently be necessary to supply heat to (or remove heat from) the system. Substituting $dQ \leqslant T\,dS$ into the relation

$$dW = dE-dQ$$

we obtain

$$dW \geqslant dE-T\,dS,$$

or since the process takes place at constant temperature this can be written as

$$dW \geqslant d(E-TS). \tag{17.1}$$

The minimum work which has to be done on the system to make it go from one state to the other is that which is required if the process is reversible, i.e. this minimum work is

$$dW = d(E-TS) = dF, \tag{17.2}$$

where

$$F = E-TS. \tag{17.3}$$

The function F is known as *the Helmholtz free energy* of the body, and we see that *the work done on the body in a reversible process at constant temperature is the change of its Helmholtz free energy.*

Suppose now that no work is done on (or by) the system; for this it is necessary in particular that the volume should remain constant (it should be understood of course that the system is not supposed to be in equilibrium, for otherwise the state of the system would be completely determined by the given values of T and V and no processes could take place at all). Equation (17.1) then becomes

$$dF \leqslant 0.$$

In other words *the Helmholtz free energy tends to a minimum in systems at constant temperature and volume,* just as the entropy tends to a maximum in closed systems. Consequently, in the state of equilibrium, F has the minimum value consistent with the given temperature and volume.

Suppose now that besides the temperature, the pressure of the system is kept constant; then evidently the volume will have to change in any process that takes place. The work done in changing the volume to keep the pressure constant will usually be done by the medium in which the system is situated, and should not be counted if we are interested in the work done on the system by some other source of work. Thus, subtracting $-p\,dV$ from (17.1) we obtain

$$dW \geqslant dE - T\,dS + p\,dV,$$

or, since T and p are constant in this case,

$$dW \geqslant d(E-TS+pV). \tag{17.4}$$

The minimum work which has to be done to produce the change of state is thus

$$dW = d(E-TS+pV) = dG, \tag{17.5}$$

where

$$G = E-TS+pV \tag{17.6}$$

is known as *the Gibbs free energy*† of the system.

† This is often called the 'thermodynamic potential', but this name is apt to be misleading, and we use 'Gibbs free energy' to bring out the similarity to 'Helmholtz free energy' (which incidentally is often called simply the 'free energy').

We can also ask what is the maximum work which can be done (on some 'object') in a change of state of the system.† In the case of processes at constant T and V, or T and p, this maximum work is evidently to be obtained from (17.2) or (17.5) by changing the sign. Thus for constant T and V

$$dW_{\max} = -dF \tag{17.7}$$

and for constant T and p

$$dW_{\max} = -dG. \tag{17.8}$$

Similarly to what we said about the Helmholtz free energy, it is easy to see that *in systems at constant temperature and pressure the Gibbs free energy tends to a minimum*, so that in equilibrium G has the minimum value consistent with the given temperature and pressure.

We shall now write down the differentials of the functions F and G. Substituting (12.3) in

$$dF = dE - T\,dS - S\,dT$$

we obtain

$$dF = -S\,dT - p\,dV, \tag{17.9}$$

from which follow

$$S = -(\partial F/\partial T)_V, \qquad p = -(\partial F/\partial V)_T. \tag{17.10}$$

By means of (17.3) and (17.10) the energy E can be expressed in terms of the Helmholtz free energy in the form

$$E = F - T\left(\frac{\partial F}{\partial T}\right)_V = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right). \tag{17.11}$$

For dG we have

$$dG = dE - T\,dS - S\,dT + p\,dV + V\,dp;$$

substituting (12.3) we find

$$dG = -S\,dT + V\,dp, \tag{17.12}$$

and similarly to (17.10),

$$S = -(\partial G/\partial T)_p, \qquad V = (\partial G/\partial p)_T. \tag{17.13}$$

Combining (17.6) and (17.13) we find

$$E = G - T\left(\frac{\partial G}{\partial T}\right)_p - p\left(\frac{\partial G}{\partial p}\right)_T. \tag{17.14}$$

If there are other parameters ξ_i besides the volume, then the thermo-

† We are not concerned here with the work done on the medium.

dynamic identities (17.9) and (17.12) assume the more general forms (analogous to 12.4)

$$dF = -S\,dT - p\,dV + \sum_i \Xi_i\,d\xi_i, \tag{17.15}$$

$$dG = -S\,dT + V\,dp + \sum_i \Xi_i\,d\xi_i. \tag{17.16}$$

If the parameters ξ_i change slightly, then F and G will also change, and the corresponding δF and δG will be equal if the former change is at constant temperature and volume, while the latter is at constant temperature and pressure. The same is true of δE and δH, if the energy changes at constant S and V, and the heat function at constant S and p (as can be seen from (12.4) and the analogous equation for W). Thus

$$(\delta E)_{S,V} = (\delta H)_{S,p} = (\delta F)_{T,V} = (\delta G)_{T,p}. \tag{17.17}$$

We shall obtain two more relations, connecting the quantity of heat absorbed during a process, with the corresponding minimum (or maximum) work. Consider first of all any process at constant temperature and volume, then as we saw in § 15 the quantity of heat, Q_V, is equal to the change of energy, while the minimum work W required to make the process take place is equal to the change of Helmholtz free energy. Since

$$E = F - T(\partial F/\partial T),$$

$$Q_V = W - T\left(\frac{\partial W}{\partial T}\right)_V = -T^2\frac{\partial}{\partial T}\left(\frac{W}{T}\right)_V. \tag{17.18}$$

If the process is at constant temperature and pressure, then the quantity of heat, Q_p, is equal to the change of the heat function (§ 15), and the minimum work to the change of Gibbs free energy. Since

$$H = G + TS = G - T(\partial G/\partial T),$$

$$Q_p = W - T\left(\frac{\partial W}{\partial T}\right)_p = -T^2\frac{\partial}{\partial T}\left(\frac{W}{T}\right)_p. \tag{17.19}$$

In conclusion we may note that at absolute zero, i.e. at $T = 0$, the free energy F is equal to the energy E. Since F has a minimum for the equilibrium state, the same must be true of E at $T = 0$; now the energy is made up of the kinetic energy of the atoms and the potential energy of their interaction, and since the former cannot be negative its minimum value is zero. Thus at $T = 0$ the atoms of a body will be at rest, while their potential energy of interaction will have its minimum value.

18. Transformation of variables

The functions E, F, G, and H are often called thermodynamic potentials or characteristic functions, in a general way, on account of their analogy to mechanical potentials, since their derivatives give the other thermodynamic quantities. In this sense E, F, G, and H are potentials with respect to the pairs of independent variables V, S; V, T; p, T; p, S, respectively. From any one of these potentials all the other thermodynamic quantities can be derived as functions of the corresponding pair of independent variables.

The most often used pairs of variables in practice are V, T and p, T, and so we often have to transform the various derivatives of the thermodynamic functions with respect to each other, to other variables, either dependent or independent.

If we transform to the pair of independent variables V, T, the result will be expressed in terms of p and C_v (both expressed as functions of V and T), while if we have to transform to the variables p, T, the result will be in terms of V and C_p (expressed as functions of p and T).

Illustrations of such transformations will be found in the examples at the end of this section, and the results of these examples are themselves of practical importance.

EXAMPLES

1. Transform the derivative $(\partial S/\partial V)_T$, the independent variables remaining V and T.

SOLUTION. By (17.10).

$$\left(\frac{\partial S}{\partial V}\right)_T = -\frac{\partial}{\partial V}\left(\frac{\partial F}{\partial T}\right)_V = -\frac{\partial^2 F}{\partial V \partial T} = -\frac{\partial^2 F}{\partial T \partial V} = -\frac{\partial}{\partial T}\left(\frac{\partial F}{\partial V}\right)_T = \left(\frac{\partial p}{\partial T}\right)_V.$$

2. Transform $(\partial S/\partial p)_T$ (variables p, T).

SOLUTION. By (17.13).

$$\left(\frac{\partial S}{\partial p}\right)_T = -\frac{\partial^2 G}{\partial p \partial T} = -\frac{\partial^2 G}{\partial T \partial p} = -\left(\frac{\partial V}{\partial T}\right)_p.$$

3. Transform $(\partial E/\partial V)_T$ (variables V, T).

SOLUTION. By (12.3) and the result of Ex. 1.

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - p = T\left(\frac{\partial p}{\partial T}\right)_V - p.$$

4. Transform $(\partial E/\partial p)_T$ (variables p, T).

SOLUTION. From (12.3) and the result of Ex. 2 we obtain

$$\left(\frac{\partial E}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T - p\left(\frac{\partial V}{\partial p}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial p}\right)_T.$$

5. Transform $(\partial H/\partial V)_T$ (variables V, T).

SOLUTION. From (15.3) and Ex. 1.

$$\left(\frac{\partial H}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T + V\left(\frac{\partial p}{\partial V}\right)_T = T\left(\frac{\partial p}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial V}\right)_T.$$

6. Transform $(\partial H/\partial p)_T$ (variables p, T).

SOLUTION. From (15.3) and Ex. 2.

$$\left(\frac{\partial H}{\partial p}\right)_T = T\left(\frac{\partial S}{\partial p}\right)_T + V = V - T\left(\frac{\partial V}{\partial T}\right)_p.$$

7. Transform $(\partial E/\partial T)_p$ (variables p, T).

SOLUTION. From (12.3).

$$\left(\frac{\partial E}{\partial T}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p - p\left(\frac{\partial V}{\partial T}\right)_p = C_p - p\left(\frac{\partial V}{\partial T}\right)_p.$$

8. Transform $(\partial H/\partial T)_V$ (variables V, T).

SOLUTION. From (15.3).

$$\left(\frac{\partial H}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V + V\left(\frac{\partial p}{\partial T}\right)_V = C_v + V\left(\frac{\partial p}{\partial T}\right)_V.$$

9. Transform $(\partial C_v/\partial V)_T$ (variables V, T).

SOLUTION. $$\left(\frac{\partial C_v}{\partial V}\right)_T = T\frac{\partial^2 S}{\partial V \partial T} = -T\frac{\partial^3 F}{\partial V \partial T^2} = T\left(\frac{\partial^2 p}{\partial T^2}\right)_V.$$

10. Transform $(\partial C_p/\partial p)_T$ (variables p, T).

SOLUTION. $$\left(\frac{\partial C_p}{\partial p}\right)_T = T\frac{\partial^2 S}{\partial p \partial T} = -T\frac{\partial^3 G}{\partial p \partial T^2} = -T\left(\frac{\partial^2 V}{\partial T^2}\right)_p.$$

11. Determine $C_p - C_v$ (variables V, T).

SOLUTION. Using the properties of Jacobians given on p. 11 we obtain

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = T\frac{\partial(S,p)}{\partial(T,p)} = T\frac{\partial(S,p)}{\partial(T,V)}\bigg/\frac{\partial(T,p)}{\partial(T,V)}$$
$$= T\left[\left(\frac{\partial S}{\partial T}\right)_V\left(\frac{\partial p}{\partial V}\right)_T - \left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial p}{\partial T}\right)_V\right]\bigg/\left(\frac{\partial p}{\partial V}\right)_T = C_v - T\left(\frac{\partial S}{\partial V}\right)_T\left(\frac{\partial p}{\partial T}\right)_V\bigg/\left(\frac{\partial p}{\partial V}\right)_T.$$

Using the result of Ex. 1, this becomes

$$C_p - C_v = -T\left(\frac{\partial p}{\partial T}\right)_V^2\bigg/\left(\frac{\partial p}{\partial V}\right)_T.$$

12. Determine $C_p - C_v$ (variables p, T).

SOLUTION. Analogously to Ex. 11 we have

$$C_v = T\left(\frac{\partial S}{\partial T}\right)_V = T\frac{\partial(S,V)}{\partial(T,V)} = T\frac{\partial(S,V)}{\partial(T,p)}\bigg/\frac{\partial(T,V)}{\partial(T,p)}$$
$$= T\left[\left(\frac{\partial S}{\partial T}\right)_p\left(\frac{\partial V}{\partial p}\right)_T - \left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial V}{\partial T}\right)_p\right]\bigg/\left(\frac{\partial V}{\partial p}\right)_T = C_p - T\left(\frac{\partial S}{\partial p}\right)_T\left(\frac{\partial V}{\partial T}\right)_p\bigg/\left(\frac{\partial V}{\partial p}\right)_T,$$

and using the result of Ex. 2

$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_p^2\bigg/\left(\frac{\partial V}{\partial p}\right)_T.$$

13. Show that $$\left(\frac{\partial p}{\partial V}\right)_S = \frac{C_p}{C_v}\left(\frac{\partial p}{\partial V}\right)_T.$$

SOLUTION. Again making use of the properties of Jacobians

$$\left(\frac{\partial p}{\partial V}\right)_S = \frac{\partial(p,S)}{\partial(V,S)} = \left\{\frac{\partial(p,S)}{\partial(p,T)}\Big/\frac{\partial(V,S)}{\partial(V,T)}\right\}\frac{\partial(p,T)}{\partial(V,T)}$$
$$= \left\{\left(\frac{\partial S}{\partial T}\right)_p\Big/\left(\frac{\partial S}{\partial T}\right)_V\right\}\left(\frac{\partial p}{\partial V}\right)_T = \frac{C_p}{C_v}\left(\frac{\partial p}{\partial V}\right)_T.$$

14. Transform $(\partial T/\partial V)_S$ to the independent variables V, T.

SOLUTION.

$$\left(\frac{\partial T}{\partial V}\right)_S = \frac{\partial(T,S)}{\partial(V,S)} = \frac{\partial(T,S)}{\partial(V,T)}\Big/\frac{\partial(V,S)}{\partial(V,T)} = -\left(\frac{\partial S}{\partial V}\right)_T\Big/\left(\frac{\partial S}{\partial T}\right)_V.$$

By the result of Ex. 1 this reduces to

$$\left(\frac{\partial T}{\partial V}\right)_S = -\frac{T}{C_v}\left(\frac{\partial p}{\partial T}\right)_V.$$

15. Transform $(\partial T/\partial p)_S$ to variables p, T.

SOLUTION.

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{\partial(T,S)}{\partial(p,S)} = \frac{\partial(T,S)}{\partial(p,T)}\Big/\frac{\partial(p,S)}{\partial(p,T)} = -\left(\frac{\partial S}{\partial p}\right)_T\Big/\left(\frac{\partial S}{\partial T}\right)_p.$$

Using the result of Ex. 2 this reduces to

$$\left(\frac{\partial T}{\partial p}\right)_S = \frac{T}{C_p}\left(\frac{\partial V}{\partial T}\right)_p.$$

16. Transform $(\partial T/\partial p)_H$ to variables p, T.

SOLUTION.

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{\partial(T,H)}{\partial(p,H)} = \frac{\partial(T,H)}{\partial(p,T)}\Big/\frac{\partial(p,H)}{\partial(p,T)} = -\left(\frac{\partial H}{\partial p}\right)_T\Big/\left(\frac{\partial H}{\partial T}\right)_p.$$

Using the result of Ex. 6 this reduces to

$$\left(\frac{\partial T}{\partial p}\right)_H = \frac{T(\partial V/\partial T)_p - V}{C_p}.$$

17. Transform $(\partial T/\partial V)_E$ to variables V, T.

SOLUTION.

$$\left(\frac{\partial T}{\partial V}\right)_E = \frac{\partial(T,E)}{\partial(V,E)} = \frac{\partial(T,E)}{\partial(T,V)}\Big/\frac{\partial(V,E)}{\partial(T,V)} = -\left(\frac{\partial E}{\partial V}\right)_T\Big/\left(\frac{\partial E}{\partial T}\right)_V.$$

Using the result of Ex. 3 this becomes

$$\left(\frac{\partial T}{\partial V}\right)_E = \frac{p - T(\partial p/\partial T)_V}{C_v}.$$

19. Rotating bodies

For a body moving as a whole relative to one system of coordinates, another coordinate system may always be found in which the body is at rest. However, we know from mechanics that this transformation from a fixed coordinate system to one moving with the bodies is equivalent to the introduction of a certain external field acting on the

body, and if the motion of the body is not uniform this equivalent field will also be variable. Now if a body is in an external field which varies with time, it will not in general be in a state of statistical equilibrium; for this reason, except for some special cases which we shall discuss below, statistics cannot be applied when the body as a whole is moving in some arbitrary manner.

These exceptions are for uniform, or uniformly accelerated progressive motion, and for uniform rotation. Uniform motion, by Galileo's relativity principle, has no effect on the dynamical properties of the system, while uniformly accelerated motion is equivalent to a constant force, proportional to and directed opposite to the acceleration, and statistics is of course applicable to a system in a constant field of force. Similarly, a uniform rotation, as is well known, affects the properties of the system in the same way as a certain constant field (giving rise to the centrifugal and Coriolis forces).

Consider a body rotating about some fixed axis with angular velocity $\mathbf{\Omega}$. If we introduce, besides the fixed coordinate system, one which rotates with the body, then the velocity $\mathbf{V}$ of any particle of the body with respect to the first of these coordinate systems is related to its velocity $\mathbf{v}$ with respect to the second by

$$\mathbf{V} = \mathbf{v}+[\mathbf{\Omega}\mathbf{r}],$$

where $\mathbf{r}$ is the radius vector to the particle in the rotating system. The kinetic energy of this particle will be

$$\tfrac{1}{2}m\mathbf{V}^2 = \tfrac{1}{2}m\mathbf{v}^2+m\mathbf{v}[\mathbf{\Omega}\mathbf{r}]+\tfrac{1}{2}m[\mathbf{\Omega}\mathbf{r}]^2$$

and hence the Lagrangian function for the whole rotating body will be

$$L = \tfrac{1}{2}\sum m\mathbf{v}^2+\sum m\mathbf{v}[\mathbf{\Omega}\mathbf{r}]+\tfrac{1}{2}\sum m[\mathbf{\Omega}\mathbf{r}]^2-U,$$

where $\sum$ denotes summation over all particles in the body (we have omitted the suffixes in $m\mathbf{v}$ and $\mathbf{r}$ for compactness), and U is the potential energy of the body. The momentum of the given particle is

$$\mathbf{p} = \partial L/\partial\mathbf{v} = m\mathbf{v}+m[\mathbf{\Omega}\mathbf{r}], \tag{19.1}$$

and the energy of the whole body in the rotating system of coordinates is

$$E'(\mathbf{v},\mathbf{r}) = \sum(\mathbf{p}\mathbf{v})-L = \tfrac{1}{2}m\mathbf{v}^2-\tfrac{1}{2}\sum m[\mathbf{\Omega}\mathbf{r}]^2+U. \tag{19.2}$$

Substituting the expression for $\mathbf{v}$ in terms of $\mathbf{p}$ ((19.1)) into (19.2) and using the rules of vector algebra, we have

$$E'(\mathbf{p},\mathbf{r}) = \tfrac{1}{2}\sum \mathbf{p}^2/m+U-\mathbf{\Omega}\sum[\mathbf{r}\mathbf{p}] = \tfrac{1}{2}\sum\mathbf{p}^2/m+U-\mathbf{\Omega}\mathbf{M}(\mathbf{p},\mathbf{r}), \tag{19.3}$$

where $\mathbf{M}(\mathbf{p},\mathbf{r}) = \sum [\mathbf{rp}]$ is the angular momentum of the whole body. The momentum of each particle in the fixed coordinate system is $m\mathbf{V}$, and by (19.1) this is equal to the momentum $\mathbf{p}$ in the rotating system. Thus the energy in the fixed coordinate system is

$$E(\mathbf{p},\mathbf{r}) = \tfrac{1}{2}\sum \mathbf{p}^2/m+U$$

and (19.3) becomes

$$E'(\mathbf{p},\mathbf{r}) = E(\mathbf{p},\mathbf{r})-\mathbf{\Omega}\mathbf{M}(\mathbf{p},\mathbf{r}). \tag{19.4}$$

From which follows

$$\frac{\partial E'(\mathbf{p},\mathbf{r})}{\partial\mathbf{\Omega}} = -\mathbf{M}(\mathbf{p},\mathbf{r}).$$

Taking mean values with respect to the coordinates and momenta and using (11.3) we find

$$(\partial E'/\partial\mathbf{\Omega})_S = -\mathbf{M}, \tag{19.5}$$

where we use the notation

$$E = \overline{E(\mathbf{p},\mathbf{r})} \quad \text{and} \quad \mathbf{M} = \overline{\mathbf{M}(\mathbf{p},\mathbf{r})}.$$

We see therefore that an extra term $-\mathbf{M}\,d\mathbf{\Omega}$ must be added to the thermodynamic identity, changing it to

$$dE' = T\,dS-\mathbf{M}\,d\mathbf{\Omega}. \tag{19.6}$$

Taking mean values on both sides of (19.4), it becomes $E' = E-\mathbf{M\Omega}$; differentiating and substituting in (19.6) we obtain

$$dE = T\,dS+\mathbf{\Omega}\,d\mathbf{M}. \tag{19.7}$$

Using (19.7), the differential of the Helmholtz free energy, $F = E-TS$ may be written as

$$dF = -S\,dT+\mathbf{\Omega}\,d\mathbf{M}. \tag{19.8}$$

In connexion with this discussion it should be noticed that if a body is rotating about some axis, which is *not* one of its axes of inertia, then, as is well known from mechanics, the axis of rotation will move about in the body. Consequently the field equivalent to the rotation will be variable, and so this cannot be a state of equilibrium; in fact rotation of this kind must be unstable, tending to change to rotation about one of the principal axes of inertia. It is easy to determine about which axis the rotation will be stable. Thus substituting $\Omega = M/I$ (I is the moment of inertia) into the relation $\partial F/\partial M = \Omega$, we obtain

$$F = F_0+\tfrac{1}{2}M^2/I, \tag{19.9}$$

where F_0 is the Helmholtz free energy when there is no rotation. Since F tends to a minimum, and M is constant (conservation of angular momentum), we see that the stable rotation will be about the axis with the greatest moment of inertia.

IV

THE GIBBS DISTRIBUTION

20. The Gibbs distribution

IN this section we shall be concerned with the determination of the distribution function for a macroscopic system in statistical equilibrium, which forms a relatively small part of some large closed system.

In § 7 it was shown that for a closed system the distribution function is constant at the points of phase space corresponding to the given values of the additive integrals of motion (the energy, momentum, and angular momentum, the last two not concerning us, however, as already explaned) and zero at all other points. In other words the probability of finding the closed system in some element of phase volume which corresponds to the given values of the additive integrals is proportional to the volume of the element.

If we separate a relatively small part (i.e. a subsystem) from the whole closed system, then the element of phase volume $d\Gamma_0$ of the whole system will be equal to the product of the volume element $d\Gamma$ of the phase space of the subsystem (itself the product of the differentials of all its coordinates and momenta), and the element $d\Gamma'$ of the phase space of the remaining part of the closed system, i.e. $d\Gamma_0 = d\Gamma\, d\Gamma'$.

We now have to find the probability of that state of the whole system for which the given subsystem is in the region $d\Gamma$ of its own phase space (i.e. of a *microscopic* state specified by given values of the coordinates and momenta of the subsystem). The microscopic state of the remaining part is of no interest here and it may be anywhere in the region $\Delta\Gamma'$ of its phase space, which corresponds to the macroscopic state of this part in the sense explained in § 7. The probability dw of this state of the subsystem is thus evidently proportional to $\Delta\Gamma' d\Gamma$, i.e.

$$dw \propto \Delta\Gamma' d\Gamma. \tag{20.1}$$

If the energy of the whole system is E_0, and that of the subsystem as a function of its coordinates and momenta $E(p, q)$, then the energy of the remaining part will be $E_0 - E(p, q)$, since on account of the quasi-independence of the subsystem, its interaction with the rest of the system may be neglected. By the definition (7.6), we may write

$$\Delta\Gamma' = e^{\sigma'},$$

where σ' is the entropy of the remaining part of the system; substituting in (20.1) we have

$$dw \propto e^{\sigma'\{E_0-E(p,q)\}}\,d\Gamma. \tag{20.2}$$

This formula holds for all cases, even when the energy $E(p,q)$ of the subsystem is comparable with E_0, but the most important case is when $E(p,q)$ is much smaller than E_0. In this case $\sigma'\{E_0-E(p,q)\}$ can be expanded as a power series in $E(p,q)$ and only the first two terms need be retained, i.e.

$$\sigma'\{E_0-E(p,q)\} = \sigma'(E_0)-E(p,q)\frac{d\sigma'(E_0)}{dE_0}+\dots .$$

Now $d\sigma'(E_0)/dE_0$ is just $1/\theta$, where θ is the temperature of the system (the temperature of all parts of the system is the same since the system is in equilibrium), and substituting in (20.2) we obtain

$$dw = Ae^{-E(p,q)/\theta}\,d\Gamma,$$

where A is a constant, not depending on p and q. Introducing the distribution function (probability density) $\rho(p,q)$, so that $dw = \rho\,d\Gamma$, we obtain

$$\rho = Ae^{-E(p,q)/\theta}. \tag{20.3}$$

This is one of the fundamental results of statistics, and gives the probability of the various states (here, of course, we mean microscopically described states, i.e. specified by the values of all the coordinates and momenta) of a macroscopic system which is a relatively small part of some large closed system. This distribution was discovered by Gibbs in 1901 and is known as the *Gibbs distribution* or the *canonical distribution.*

The product $\rho\,d\Gamma$ is the probability that the momenta and coordinates of the system have values in the region $d\Gamma$, and so the probability that the energy of the system has a value in the range $E(p,q)$ to $E(p,q)+dE(p,q)$ is

$$w(E)\,dE = \rho\frac{d\Gamma}{dE}\,dE.$$

This probability density for the energy, i.e. $\rho\,d\Gamma/dE$, has a sharp maximum where the energy has its mean value.

In § 6 it was explained that the logarithm of the distribution function must be an additive integral of motion, and it is easy to show that the Gibbs distribution satisfies this requirement. In fact, $E(p,q)$ is an integral of motion for the given subsystem (on account of its quasi-independence) and, moreover, additive, since the energy for several subsystems is the sum of the separate energies (the

interaction energies being negligible on account of the quasi-independence). At the same time the temperature θ is the same for all parts of the closed system, and therefore, since

$$\log \rho = \log A - E(p, q)/\theta,$$

$\log \rho$ is itself an additive integral of motion.

The constant A in (20.3) is determined by the normalization condition

$$\int \rho \, d\Gamma = A \int e^{-E(p,q)/\theta} \, d\Gamma = 1, \tag{20.4}$$

where the integration is extended over all possible values of the coordinates and momenta, and thus

$$A = 1 \Big/ \int e^{-E(p,q)/\theta} \, d\Gamma. \tag{20.5}$$

With the help of (20.3) we can determine the mean value of any physical quantity $M(p, q)$ which is a function of the coordinates and momenta of the system. Thus

$$\bar{M} = A \int M(p, q) e^{-E(p,q)/\theta} \, d\Gamma, \tag{20.6}$$

and substituting (20.5)

$$\bar{M} = \frac{\int M(p, q) e^{-E(p,q)/\theta} \, d\Gamma}{\int e^{-E(p,q)/\theta} \, d\Gamma}. \tag{20.7}$$

In particular, the mean energy (which we agreed earlier to denote simply by E, without a bar) is

$$E = \frac{\int E(p, q) e^{-E(p,q)/\theta} \, d\Gamma}{\int e^{-E(p,q)/\theta} \, d\Gamma}.$$

In the foregoing discussion it was implied that a system to which the Gibbs distribution could be applied must be a small part of a larger closed system (or that it could be made such a part), but always itself a macroscopic system. This allowed the possibility of considering the system as quasi-independent, i.e. of neglecting its interaction with the other parts of the closed system. However, it was also pointed out in § 6 that it is possible to have quasi-independent systems which are not macroscopic, and evidently all the foregoing results are applicable to such systems.

In fact the molecules of a *perfect gas* are quasi-independent systems of this kind, since although not macroscopic, their interactions are by definition negligible. This condition is satisfied by any gas consisting of molecules whose interactions fall off sufficiently rapidly

with their distances of separation (this is always the case if gravitational forces can be neglected), provided that the volume occupied by the gas is so large that at any instant the number of pairs of molecules close to each other is only a very small proportion of the total number of molecules (i.e. provided the gas is sufficiently 'dilute'). In spite of the fact that each of the molecules has only a small number of degrees of freedom, and so is in no sense a macroscopic system, (20.3) is nevertheless applicable as the Gibbs distribution function for each of the molecules (the distribution applies also, of course, to the gas as a whole, considering it as a single macroscopic system forming a part of some closed system). If we denote the energy of a molecule by ϵ, then the distribution function for this molecule has the form

$$\rho = ae^{-\epsilon/\theta}, \tag{20.8}$$

and $\rho\, d\tau$ is the probability of finding this molecule in the volume element $d\tau$ of its own phase space ($d\tau$ is the product of the differentials of all the momenta and coordinates of this molecule).

At any instant of time the molecules will be distributed in phase space so that a certain number (regardless of their identity) will be found in any particular element of phase space. These numbers may in general vary with time, but if the gas is in a state of statistical equilibrium, then, nearly always (for an overwhelming proportion of any sufficiently long time), the number of molecules in any particular element will be practically constant, and equal to the mean value of this number (provided this element contains sufficiently many molecules).

We shall denote the mean number of molecules in the element $d\tau$ by $dN = n\, d\tau$, where n is the 'density' of molecules in phase space. It is evident that this number will be the product of the probability that any one molecule should be in this volume element, and N, the total number of molecules in the gas, i.e.

$$dN = n\, d\tau = N\rho\, d\tau, \tag{20.9}$$

or $n = N\rho$. Substituting the value of ρ from (20.8) we obtain

$$n = ce^{-\epsilon/\theta}, \tag{20.10}$$

where c is a constant, determined by the condition that the total number of molecules in the gas is N, i.e.

$$\int n\, d\tau = N. \tag{20.11}$$

The equation (20.10) is known as *Boltzmann's distribution* (it was discovered by Boltzmann in 1877), and we may emphasize again that it refers to the individual molecules of an ideal gas.

The mean value of any quantity $M(p,q)$ characteristic of a single molecule (e.g. its energy or velocity) is evidently

$$\bar{M} = \frac{1}{N}\int M(p,q)n(p,q)\,d\tau. \tag{20.12}$$

In conclusion we must point out an important fact. The energy $E(p,q)$ or ϵ in (20.3) or (20.10) is the *total* energy of the body (or molecule) and includes *inter alia* the internal energy of the atoms. The potential energy of interaction of the electrons with the nucleus of an atom has the form $-a/r$, where r is the distance between an electron and the nucleus. Thus in the expressions (20.3) or (20.10) there will be a factor $e^{a/r\theta}$, which becomes infinite for $r = 0$, and so makes the probability ρ also infinite, or, in other words, the electrons should fall into the nucleus. The fact that this does not really happen is one of many results which show that classical mechanics is not applicable to processes in the interior of the atom. On this account we have, in classical statistics, to consider atoms simply as material points, without taking any account of their structure.

EXAMPLE

Deduce the Gibbs distribution from the condition of maximum entropy for a closed system in statistical equilibrium.

SOLUTION. In the state of statistical equilibrium the entropy of a closed system has a maximum value, for a given value of the total energy. The equilibrium state is characterized by definite mean values for the energies of each of the parts of the system (subsystems), and so the condition of maximum entropy for the closed system may be replaced by the condition that the entropies of each of the subsystems should be a maximum, for the given mean values of their energies. Let $\rho(p,q)$ be the distribution for one of the subsystems, then its entropy will be given by (7.9)

$$\sigma = \int \rho \log\frac{1}{\rho}\,d\Gamma. \tag{a}$$

This must have a maximum, subject to the condition that the mean energy of the subsystem is

$$E = \int \rho E(p,q)\,d\Gamma, \tag{b}$$

and the normalization condition

$$1 = \int \rho\,d\Gamma. \tag{c}$$

Following Lagrange's method we multiply the variations of the integrals

(b) and (c) by constants β and $(1+\alpha)$, add in the variation of (a), and equate to zero, giving

$$\int \left[\log\frac{1}{\rho}+\alpha+\beta E(p,q)\right]\delta\rho d\Gamma = 0.$$

In order that this should be identically satisfied we must have

$$\log(1/\rho)+\alpha+\beta E(p,q) = 0,$$

from which we obtain the distribution function of the subsystem in the equilibrium state as

$$\rho = e^{\alpha+\beta E(p,q)},$$

which is evidently identical with (20.3) if we write

$$e^{\alpha} = A, \qquad \beta = -1/\theta.$$

21. The Maxwell distribution

The energy of a system as a function of its coordinates and momenta can be considered (for a system obeying the laws of classical mechanics) as the sum of a kinetic and a potential energy; the former is a quadratic function of the momenta,† while the latter is a function of the coordinates, whose form depends on the law of interaction of the particles composing the system and the external field in which the system is placed. Denoting the kinetic and potential energies by $K(p)$ and $U(q)$ respectively, we have $E(p,q) = K(p)+U(q)$, and the exponential in the Gibbsian distribution breaks up into two factors

$$e^{-E/\theta} = e^{-U/\theta}e^{-K/\theta},$$

of which one depends only on the coordinates and the other only on the momenta. In the same way the volume element of phase space $d\Gamma$, can be considered as the product of two factors

$$d\Gamma = d\Gamma_q d\Gamma_p,$$

one of which contains only differentials of the coordinates

$$(d\Gamma_q = dq_1 \dots dq_n)$$

and the other differentials of the momenta $(d\Gamma_p = dp_1 \dots dp_n)$. Thus the probability of a volume element $d\Gamma$ of phase space becomes

$$dw(p,q) = Ae^{-U(q)/\theta}d\Gamma_q e^{-K(p)/\theta}d\Gamma_p.$$

According to the multiplication theorem of probability, this means that *the probabilities of the momenta and of the coordinates are independent of each other*, in the sense that the particular values of the coordinates have no influence on the probabilities of various values

† It is assumed that we are using Cartesian coordinates.

of the momenta, and vice versa. Thus the probability of any values of the momenta is proportional to $e^{-K(p)/\theta}\,d\Gamma_p$, or

$$dw_p(p) = ae^{-K(p)/\theta}\,d\Gamma_p, \qquad (21.1)$$

and similarly the probability for a value of the coordinates is

$$dw_q(q) = be^{-U(q)/\theta}\,d\Gamma_q. \qquad (21.2)$$

Thus the expressions $\rho_p(p) = ae^{-K/\theta}$ and $\rho_q(q) = be^{-U/\theta}$ can be interpreted as the probability densities for the momenta and coordinates respectively.

Since the sum of the probabilities of all possible values of the momenta must be unity (and similarly for the coordinates), the probabilities dw_p and dw_q must be normalized separately, i.e. their integrals over all possible values of the momenta and coordinates respectively, must each be unity. The values of a and b in (21.1) and (21.2) can then be determined from these normalization conditions.

We shall first of all consider the probability distribution for the momenta, and we must emphasize again that the form of this distribution is entirely independent of the type of interaction of the particles within the system, and of the external field, and so is valid for any system whatever.

The kinetic energy of the whole system is equal to the sum of the kinetic energy of all its component atoms, so the probability again splits up into a number of factors, each of which depends on the velocities of only a single atom. Just as before, this means that the *probabilities of the momenta (or velocities) of different atoms are independent of each other*, and so the velocity of one of them has no influence whatever on the probability of velocities for the others. Thus the probability distribution of velocities can be written down for any individual atom.

For an atom of mass m the kinetic energy is

$$K = (p_x^2+p_y^2+p_z^2)/2m = \tfrac{1}{2}m(v_x^2+v_y^2+v_z^2),$$

where v_x, v_y, v_z and p_x, p_y, p_z are the Cartesian components of the velocity and momentum respectively, and so the probability distribution assumes the form

$$dw = ce^{-(p_x^2+p_y^2+p_z^2)/2m\theta}\,dp_x\,dp_y\,dp_z = cm^3e^{-\frac{1}{2}m(v_x^2+v_y^2+v_z^2)/\theta}\,dv_x\,dv_y\,dv_z.$$

(since $p_x = mv_x$, etc). The constant c is determined by the normalization condition that the sum of the probabilities of all values of

p_x, p_y, p_z should be unity. Since p_x, p_y, p_z can assume all values from $-\infty$ to ∞, we obtain for c the equation

$$c\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty}\int\limits_{-\infty}^{\infty} e^{-(p_x^2+p_y^2+p_z^2)/2m\theta}\,dp_x\,dp_y\,dp_z = c\Big[\int\limits_{-\infty}^{\infty} e^{-p^2/2m\theta}\,dp\Big]^3$$

$$= c(2m\pi\theta)^{\frac{3}{2}} = 1,\dagger$$

hence $c = (2\pi m\theta)^{-\frac{3}{2}}$, and we obtain finally the following distribution function for the velocities:

$$dw = \left(\frac{m}{2\pi\theta}\right)^{\frac{3}{2}} e^{-\frac{1}{2}m(v_x^2+v_y^2+v_z^2)/\theta}\,dv_x\,dv_y\,dv_z, \qquad (21.3)$$

which is known as the Maxwell distribution.‡

With the help of the Maxwell distribution it is possible to calculate the mean value of any function of the velocities, the probability of various ranges of the velocities, and so on, and some examples will be found at the end of this section. We may note incidentally that the expression (21.3) itself splits up into three independent factors ($dw_{v_x} = (m/2\pi\theta)^{\frac{1}{2}}e^{-\frac{1}{2}mv_x^2/\theta}\,dv_x$, etc.) which shows that the probability of each component of the velocity is independent of the other components.

If the system consists of molecules (for instance, a polyatomic gas), then the Maxwell distribution applies not only to the individual atoms but also to the progressive motion of the molecules, i.e. to the motion of their centres of gravity. In fact, we know from mechanics that the kinetic energy of a molecule can be expressed as the sum of its kinetic energy of progressive motion $\frac{1}{2}mv^2$ (m being the mass of the molecule and v the velocity of its centre of gravity), and the energies of relative motion of the atoms within the molecule. Thus the probability for the velocities of the molecules may be expressed as the product of the probability of its progressive velocity and the probabilities of the relative velocities of the atoms within the molecule. The first of these factors will have the form (21.3), where m will now mean the total mass of the molecule and v_x, v_y, v_z the components of velocity of the centre of gravity.

Equation (21.3) is expressed in Cartesian coordinates in 'velocity

† By the well-known formula (see footnote on p. 59) $\int\limits_{-\infty}^{\infty} e^{-ax^2}\,dx = \sqrt{(\pi/a)}$. We may incidentally notice that from the normalization condition it follows again that the temperature θ cannot be negative since otherwise the integral would not converge.

‡ It was discovered by Maxwell in 1860, before the discovery of the Gibbs distribution.

space', and if it is transformed to spherical polar coordinates we obtain

$$dw = (m/2\pi\theta)^{\frac{3}{2}} e^{-\frac{1}{2}mv^2/\theta} v^2\,dv \sin\vartheta\,d\vartheta d\phi, \tag{21.4}$$

where v is the absolute value of the velocity and ϑ and ϕ the polar angles determining its direction. Integrating over the angles we thus find the probability distribution for the absolute values of the velocity:

$$dw_v = 4\pi(m/2\pi\theta)^{\frac{3}{2}} e^{-\frac{1}{2}mv^2/\theta} v^2\,dv. \tag{21.5}$$

It is sometimes convenient to use cylindrical coordinates in 'velocity space', we then have the distribution

$$dw = (m/2\pi\theta)^{\frac{3}{2}} e^{-\frac{1}{2}m(v_z^2+v_r^2)/\theta} v_r\,dv_r\,dv_z\,d\phi, \tag{21.6}$$

where v_z is the component of v along the z-axis, v_r the component perpendicular to the z-axis, and ϕ the angle determining the direction of the latter component.

If the system is a perfect gas, consisting of N identical molecules, then instead of the probability distribution for the velocity, we can write down the number of molecules with velocities in the given range (i.e. between v_x, v_y, v_z and v_x+dv_x, v_y+dv_y, v_z+dv_z, or between v and $v+dv$). If the gas is polyatomic, then by 'velocity' we mean the velocity of the centre of gravity of a molecule, and by coordinates we mean the coordinates of the centre of gravity.

Suppose that the gas is *not* in an external field of force. Then (20.9) and (20.10) give the number of molecules having momenta and coordinates in the given ranges as

$$dN = ce^{-(p_x^2+p_y^2+p_z^2)/2m\theta}\,dp_x\,dp_y\,dp_z\,dxdydz.$$

If the gas is polyatomic, then $d\tau$ contains the differentials of *all* the momenta and coordinates, not only those of the centre of gravity of the molecule; we can, however, integrate over all the others (since we are concerned at present only with the distribution as regards momenta and coordinates of the centre of gravity), and so obtain some constant which is absorbed into the original constant in (20.10) which arose from the normalization condition.

The constant c in the above equation is determined quite analogously to the constant in (21.3). The integration over $dxdydz$ is extended over the whole volume V occupied by the gas, and so simply gives the result V, since there are no functions of x, y, z in the integral. We thus obtain, replacing θ by kT,

$$dN = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-m(v_x^2+v_y^2+v_z^2)/2kT}\,dv_x\,dv_y\,dv_z\,dxdydz \tag{21.7}$$

as the number of molecules in the volume element $dxdydz$ having velocities in the range $dv_x dv_y dv_z$.

In a similar way to that by which we obtained (20.4) from (20.3) we can obtain the distribution of molecules as regards absolute velocities, i.e.

$$dN_v = \frac{4\pi N}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-mv^2/2kT} v^2\, dv\, dxdydz. \tag{21.8}$$

Various applications of these results will be found in the examples.

EXAMPLES

1. Find the mean values of the squares of the Cartesian components of velocities.

SOLUTION. By (21.3) and the definition of mean values we obtain†

$$\overline{v_x^2} = \iiint\limits_{-\infty}^{\infty} v_x^2 \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-m(v_x^2+v_y^2+v_z^2)/2kT}\, dv_x\, dv_y\, dv_z$$
$$= \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int\limits_{-\infty}^{\infty} v_x^2\, e^{-mv_x^2/2kT}\, dv_x \int\limits_{-\infty}^{\infty} e^{-mv_y^2/2kT}\, dv_y \int\limits_{-\infty}^{\infty} e^{-mv_z^2/2kT}\, dv_z = \frac{kT}{m}.$$

2. Find the mean value of the nth power of the absolute value of the velocity.

SOLUTION. By (21.5) we have

$$\overline{v^n} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \int\limits_0^{\infty} e^{-mv^2/2kT} v^{n+2}\, dv = \frac{2}{\sqrt{\pi}}\left(\frac{m}{2kT}\right)^{-\frac{1}{2}n} \Gamma\{\tfrac{1}{2}(n+3)\}.$$

In particular if $n = 2r$ (r an integer)

$$\overline{v^{2r}} = (kT/m)^r (2r+1)!!,$$

while if $n = 2r+1$, $\quad \overline{v^{2r+1}} = \frac{2}{\sqrt{\pi}}\left(\frac{2kT}{m}\right)^{\frac{1}{2}(2r+1)} (r+1)!.$

† The integrals occurring in this and the following examples, of the form $\int\limits_0^{\infty} e^{-ax^2} x^n\, dx$, may be evaluated as follows. Substitution of $ax^2 = y$ gives

$$\int\limits_0^{\infty} e^{-ax^2} x^n\, dx = \frac{1}{2a^{\frac{1}{2}(n+1)}} \int\limits_0^{\infty} e^{-y} y^{\frac{1}{2}(n-1)}\, dy = \frac{1}{2a^{\frac{1}{2}(n+1)}} \Gamma\{\tfrac{1}{2}(n+1)\}.$$

In particular if $n = 2r$ and r is an integer > 0, then

$$\int\limits_0^{\infty} e^{-ax^2} x^{2r}\, dx = \frac{(2r-1)!!}{2^{r+1}} \sqrt{\frac{\pi}{a^{2r+1}}}.$$

where $(2r-1)!!$ denotes the product $1.3.5...(2r-1)$.

If $n = 0$, then $\quad \int\limits_0^{\infty} e^{-ax^2}\, dx = \frac{1}{2}\sqrt{(\pi/a)}$.

If $n = 2r+1$, then $\quad \int\limits_0^{\infty} e^{-ax^2} x^{2r+1}\, dx = r!/2a^{r+1}$.

The same integral between the limits $-\infty$ and $+\infty$ is zero in the last case ($n = 2r+1$) and double the integral between 0 and ∞ in the first two cases.

3. Find the fluctuation of the velocity.

SOLUTION. By (2.5) the square of the fluctuation of velocity is

$$\overline{(v-\bar{v})^2} = \overline{(\Delta v)^2} = \overline{v^2}-(\bar{v})^2.$$

Applying the result of Ex. 2 for $n = 1$ and $n = 2$ we find

$$\overline{(\Delta v)^2} = (kT/m)(3-8/\pi).$$

4. Find the mean energy, the mean square energy, and the fluctuation of the energy of the molecules of a perfect gas.

SOLUTION. For a monatomic gas $\epsilon = \frac{1}{2}mv^2$, thus by Ex. 2

$$\bar{\epsilon} = \tfrac{1}{2}m\overline{v^2} = \frac{3kT}{2}, \qquad \overline{\epsilon^2} = \tfrac{1}{4}m^2\overline{v^4} = \tfrac{15}{4}k^2T^2,$$

$$\overline{(\Delta\epsilon)^2} = \overline{\epsilon^2}-(\bar{\epsilon})^2 = \tfrac{3}{2}k^2T^2.$$

5. Find the distribution of molecules of a monatomic gas with respect to energy (i.e. the number of molecules having energies between ϵ and $\epsilon+d\epsilon$).

SOLUTION. Substituting $v = \sqrt{(2\epsilon/m)}$ in (21.8) and integrating over $dxdydz$ we find

$$dN_\epsilon = N\frac{2}{(\pi k^3T^3)^{\frac{1}{2}}}e^{-\epsilon/kT}\sqrt{\epsilon}\,d\epsilon.$$

22. Collisions with the walls of the vessel

The molecules of a gas contained in a vessel will in general frequently collide with the walls of the vessel, and with the help of the results of the previous section we can calculate how many collisions take place per unit time over unit area of the walls.

Let the coordinate system be such that the z-axis is normal to some element of area of the wall of the vessel, which we can then denote by $dxdy$; of the molecules with a given z-component of velocity, only those at a distance $z \leq v_z$ will reach the wall and therefore collide with it in unit time (v_z is of course the velocity component *towards* the wall). Thus the number of collisions dn per unit time per unit area of molecules whose velocity components are in the range v_x, v_y, v_z to v_x+dv_x, v_y+dv_y, v_z+dv_z, can be obtained by integrating (21.7) with respect to z between the limits 0 and v_z, and integrating $dxdy$ over the unit area. We find

$$dn = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-m(v_x^2+v_y^2+v_z^2)/2kT}v_z\,dv_x\,dv_y\,dv_z; \qquad (22.1)$$

this formula gives us the number of collisions as a function of the velocity components.

From (22.1) it is easy to find the total number n of collisions of the molecules of a perfect gas with unit area in unit time. Integrating (22.1) over the velocity v_z from 0 to ∞ and over v_x and v_y from $-\infty$ to ∞

(the range from $-\infty$ to 0 of v_z must not be included, since it covers those molecules moving *away* from the wall), we find

$$n = \frac{N}{V}\left(\frac{kT}{2\pi m}\right)^{\frac{1}{2}}. \tag{22.2}$$

Equation (22.1) can also be written in spherical polar coordinates in velocity space; thus taking the z-axis as the polar axis, $v_z = v\cos\vartheta$, and

$$dn = \frac{N}{V}\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mv^2/kT} v^3\, dv \sin\vartheta \cos\vartheta\, d\vartheta d\phi. \tag{22.3}$$

EXAMPLES

1. Find the number of collisions with unit area of the wall in unit time of molecules striking it at an angle between ϑ and $\vartheta+d\vartheta$ to the normal.

SOLUTION. $$dn_\vartheta = \frac{N}{V}\left(\frac{2kT}{m\pi}\right)^{\frac{1}{2}} \sin\vartheta\cos\vartheta\, d\vartheta.$$

2. Find the number of collisions with unit area of the wall in unit time of molecules whose velocities lie between v and $v+dv$.

SOLUTION. $$dn_v = \frac{N}{V}\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} e^{-\frac{1}{2}mv^2/kT} v^3\, dv.$$

3. Find the total energy, E_{coll}, of the molecules of monoatomic gas striking unit area of the wall in unit time.

SOLUTION. $$E_{coll} = \frac{N}{V}\left(\frac{2k^3T^3}{m\pi}\right)^{\frac{1}{2}}.$$

4. Find the total momentum of the molecules striking unit area of the wall in unit time.

SOLUTION. $p_{x\,coll} = p_{y\,coll} = 0, \qquad p_{z\,coll} = NkT/2V.$

23. Collisions of the molecules with each other

We shall now find the number of collisions per unit time of the molecules of a perfect gas, not with the vessel, but with one particular molecule. To do this we must first of all find the distribution of molecules as regards their relative velocities to each other; we pick out some particular molecule and consider the motion of the other molecules relative to this one. We know from mechanics that the kinetic energy of relative motion of two particles of masses m_1 and m_2 is $\frac{1}{2}\mu v'^2$, where $\mu = m_1 m_2/(m_1+m_2)$ is the reduced mass, and v' the relative velocity. Consequently the distribution of the molecules of a perfect gas with respect to the relative velocities and the coordinates of the centre of gravity has the same form as (21.5) except that μ has to be substituted for m. Since all the molecules are identical,

$\mu = \frac{1}{2}m$, and we have for the number of molecules per unit volume whose velocities relative to the particular molecule lie between v' and $v'+dv'$

$$dN = \frac{N}{V}\frac{\pi}{2}\left(\frac{m}{\pi kT}\right)^{\frac{3}{2}} e^{-mv'^2/4kT} v'^2\,dv'. \tag{23.1}$$

The collisions of molecules with each other are accompanied by various processes, for instance deviation (scattering) through some angle, dissociation into atoms, etc., and it is usual to describe such processes by an *effective cross-section.* This is defined for any process occurring during collisions between a given molecule and the others, as the ratio of the probability per unit time of a collision accompanied by this process, to the 'flux density' of particles of the particular relative velocity (the flux density is defined as the number of molecules per unit volume multiplied by the corresponding velocity). Thus the number of collisions per unit time of molecules with the given molecule, accompanied by some process of effective cross-section σ is

$$n = \int\limits_0^\infty \frac{N\pi}{2V}\left(\frac{m}{\pi kT}\right)^{\frac{3}{2}} \sigma e^{-mv'^2/4kT} v'^3\,dv'. \tag{23.2}$$

EXAMPLE

Find the number of collisions of the molecules with one particular molecule, the molecules being considered as hard spheres of radius r.

SOLUTION. The effective cross-section for collisions of the molecules with each other will in this case be $\sigma = \pi(2r)^2 = 4\pi r^2$ (independently of what processes may accompany the collision; a collision takes place if one molecule passes another with their centres less than or equal to $2r$ apart). Substituting in (23.2) we find

$$n' = 16r^2\frac{N}{V}\left(\frac{\pi kT}{m}\right)^{\frac{1}{2}}.$$

24. Rotation of molecules

Just as we obtained the Maxwell distribution for the progressive motion of molecules, we can discuss also their rotational motion. If, as is usually the case, the vibrations inside the molecule are not appreciable, the rotation of a molecule can be considered as the rotation of a rigid body.

Let the principal moments of inertia be I_1, I_2, and I_3, then the kinetic energy of rotation of a molecule is

$$\epsilon_{\text{rot}} = \tfrac{1}{2}(I_1\Omega_1^2 + I_2\Omega_2^2 + I_3\Omega_3^2),$$

where Ω_1, Ω_2, Ω_3 are the components of the angular velocity along the axes of inertia. The components of the angular momentum are

$$M_1 = I_1\Omega_1, \qquad M_2 = I_2\Omega_2, \qquad M_3 = I_3\Omega_3.$$

Since the energy in the Gibbs distribution must be expressed as a function of coordinates and momenta, we write ϵ_{rot} in the form

$$\epsilon_{\mathrm{rot}} = \frac{M_1^2}{2I_1}+\frac{M_2^2}{2I_2}+\frac{M_3^2}{2I_3}.$$

Since, moreover, the rotational energy enters additively into the total kinetic energy of the molecule, the probability for the angular momentum is independent of the probabilities of the ordinary momenta and can be expressed separately as

$$dw = A\exp\left[-\frac{1}{2kT}\left(\frac{M_1^2}{I_1}+\frac{M_2^2}{I_2}+\frac{M_3^2}{I_3}\right)\right]dM_1\,dM_2\,dM_3.$$

The normalization condition determines A as

$$A = (2\pi kT)^{-\frac{3}{2}}(I_1 I_2 I_3)^{-\frac{1}{2}},$$

so that

$$dw = (2\pi kT)^{-\frac{3}{2}}(I_1 I_2 I_3)^{-\frac{1}{2}}\exp\left[-\frac{1}{2kT}\left(\frac{M_1^2}{I_1}+\frac{M_2^2}{I_2}+\frac{M_3^2}{I_3}\right)\right]dM_1\,dM_2\,dM_3. \tag{24.1}$$

Going over from M_1, M_2, M_3 to Ω_1, Ω_2, Ω_3 we can also write

$$dw = (2\pi kT)^{-\frac{3}{2}}(I_1 I_2 I_3)^{\frac{1}{2}}\exp\left[-\frac{1}{2kT}(I_1\Omega_1^2+I_2\Omega_2^2+I_3\Omega_3^2)\right]d\Omega_1\,d\Omega_2\,d\Omega_3. \tag{24.2}$$

If the molecule has the form of a straight line, we can consider rotation only about the two axes perpendicular to this straight line. Denoting the moment of inertia about an axis perpendicular to the straight line by I, it is easy to deduce that

$$dw = (2\pi kTI)^{-1}e^{-M^2/2IkT}\,dM_1\,dM_2 = (I/2\pi kT)e^{-I\Omega^2/2kT}\,d\Omega_1\,d\Omega_2, \tag{24.3}$$

where $M^2 = M_1^2+M_2^2$ and $\Omega^2 = \Omega_1^2+\Omega_2^2$.

EXAMPLES

1. Find the mean value of the square of the absolute value of the angular velocity of rotation of a molecule.

SOLUTION. $$\overline{\Omega^2} = \tfrac{1}{2}kT\left(\frac{1}{I_1}+\frac{1}{I_2}+\frac{1}{I_3}\right).$$

2. Find the mean value of the square of the absolute value of the angular momentum of a molecule.

SOLUTION. $$\overline{M^2} = \tfrac{1}{2}kT(I_1+I_2+I_3).$$

25. Rotating bodies

In order to obtain the Gibbs distribution for a body rotating as a whole, we must consider it in the rotating system of coordinates with respect to which it is at rest. As was shown in § 19, the energy E' of the body in this frame of reference is

$$E' = \sum \tfrac{1}{2}mv^2 + U - \sum \tfrac{1}{2}m[\mathbf{\Omega r}]^2$$

or

$$E' = E_0(\mathbf{v}, \mathbf{r}) - \sum \tfrac{1}{2}m[\mathbf{\Omega r}]^2,$$

where

$$E_0 = \sum \tfrac{1}{2}mv^2 + U$$

is independent of $\mathbf{\Omega}$.

Consequently the Gibbs distribution for a rotating body is

$$\rho\, d\Gamma = Ae^{-(E_0 - \sum \frac{1}{2}m[\mathbf{\Omega r}]^2)/kT}\, dx_1\, dy_1\, dz_1 \ldots dp_{1x}\, dp_{1y}\, dp_{1z} \ldots .$$

From the relation $\mathbf{p} = m\mathbf{v} + m[\mathbf{\Omega r}]$ (see (19.1)) we see that $dp_{1x} = m\, dv_{1x}$, etc., since in taking differentials of momenta, the coordinates must be considered as constant. Consequently

$$\rho\, d\Gamma = Be^{-(E_0 - \sum \frac{1}{2}m[\mathbf{\Omega r}]^2)/kT}\, dx_1\, dy_1\, dz_1 \ldots dv_{1x}\, dv_{1y}\, dv_{1z} \ldots . \quad (25.1)$$

Thus the Gibbs distribution with respect to coordinates and velocities for a rotating body differs from the corresponding distribution for a non-rotating body, only in the addition of a potential energy $-\sum \frac{1}{2}m[\mathbf{\Omega r}]^2$ depending only on the coordinates.

In other words the statistical properties of the body are affected in the same way as by an external field which corresponds to the centrifugal force; the Coriolis force has no influence on the statistical properties.†

26. A perfect gas in an external field of force

The formulae (21.7) and (21.8) were deduced for a perfect gas in no external field; if, however, there is such a field, we must substitute for ϵ in the general formula (20.10) for the Boltzmann distribution, the sum of ϵ_k the kinetic energy, ϵ_i the potential energy of interaction of the atoms inside a molecule, and u the potential energy of a molecule in the external field:

$$\epsilon = \epsilon_k + \epsilon_i + u.$$

The kinetic energy ϵ_k depends, of course, only on the momenta, and ϵ_i only on the relative coordinates of the atoms within the molecule; as regards u, however, it may in general depend on all the

† It should be noticed that this result is not a thermodynamic relation, and does not remain true in quantum statistics.

coordinates. Nevertheless, in the majority of cases (for instance the gravitational field) u can be assumed to depend only on the coordinates of the centre of gravity of the molecule, which we denote by x, y, z. (It is just these coordinates, of course, which do not enter into ϵ_i.)

The number of molecules in the phase volume $d\tau$ will be by (20.9) and (20.10)

$$dN = ce^{-(\epsilon_\kappa+\epsilon_i+u)/kT}\,d\tau.$$

To find the distribution of the molecules as regards only x, y, z, the coordinates of the centre of gravity, this expression must be integrated over all the differentials in $d\tau$ except $dxdydz$. Since u is the only quantity depending on x, y, z, we obtain

$$dN_{xyz} = n_0\,e^{-u(x,y,z)/kT}\,dxdydz, \tag{26.1}$$

where n_0 is a constant, arising as a result of the integration.

Thus, for a gas in statistical equilibrium and in a uniform external field, the density of molecules in space is

$$n = n_0\,e^{-u(x,y,z)/kT} \tag{26.2}$$

and n_0 is evidently the density at the place where $u(x,y,z) = 0$. The equation (26.1) or (26.2) is known as *Boltzmann's equation.*

Suppose that the external field is such that $u(x,y,z)$ becomes zero, or has some finite value, at infinity, then from (26.1) we see that in either case, the density of molecules will have a finite value at infinity (equal to $n_0\,e^{-u_\infty/kT}$). However, a finite quantity of gas cannot be spread over an infinite volume with a non-zero density, and this means that in a field of this kind a gas cannot be in equilibrium and will be continuously escaping into space. In other words the external field is not able to collect the gas into a finite volume. This applies in particular to the earth's atmosphere, since the earth's gravitational field is zero at an infinite distance; consequently the earth's atmosphere cannot be in statistical equilibrium and must continuously escape into space; this dissipation of the atmosphere is, however, so slight that it can in practice be completely neglected.

EXAMPLES

1. Find the number of molecules in the earth's field of gravity contained in an infinite cone with its apex on the earth's surface, angle 2α at the apex, and its axis vertical. The temperature of the gas to be assumed constant.

SOLUTION. The number of molecules in the volume $dxdydz$ is by (26.2)

$$n_0\,e^{-mgz/kT}\,dxdydz$$

(we assume the potential energy of a molecule to be mgz at height z above the

earth, so that n_0 is the density of molecules at $z = 0$. Transforming to cylindrical coordinates r, z, ϕ and integrating over the whole volume of the cone we obtain

$$N = \int_{\phi=0}^{2\pi} \int_{z=0}^{\infty} \int_{r=0}^{z\tan\alpha} n_0 e^{-mgz/kT} r \, d\phi dz dr = 2\pi n_0 \left(\frac{kT}{mg}\right)^3 \tan^2\alpha.$$

2. Find the density of molecules of a gas in a cylinder of radius R and length l, rotating about its axis with angular velocity Ω (total number of molecules $= N$).

SOLUTION. It was shown in § 25 that the rotation of the system as a whole is equivalent to an external field, depending only on the distance r from the axis of rotation; the potential energy in this field is the 'centrifugal' energy $-\frac{1}{2}m\Omega^2r^2$. The number of molecules in the volume element $r\,drdzd\phi$ (we use cylindrical coordinates with the z-axis along the axis of the cylinder) is

$$dN = Ae^{\frac{1}{2}m\Omega^2r^2/kT} r \, drdzd\phi.$$

The constant A is determined by the normalization condition that the total number of molecules should be N, and we obtain finally the density of molecules n as

$$n = \frac{Nm\Omega^2}{2\pi kTl(e^{\frac{1}{2}m\Omega^2R^2/kT}-1)} e^{\frac{1}{2}m\Omega^2r^2/kT}.$$

V

DETERMINATION OF THE THERMODYNAMIC FUNCTIONS

27. General formulae

ALL the relations deduced in Chapter III referred to arbitrary macroscopic systems, independently of their actual properties. In this chapter we shall evaluate the various thermodynamic functions occurring in these relations for some actual physical systems.

It is first of all necessary, however, to obtain the relation between the constant A entering in the Gibbs distribution (20.3) and the thermodynamic functions. To do this we substitute (20.3) into the definition of entropy $\sigma = \overline{\log 1/\rho}$ and obtain

$$\sigma = -\log A + \overline{E(p,q)}/\theta.$$

Rewriting this with the usual abbreviation of E for $\overline{E(p,q)}$, the mean energy, we have

$$\log A = (E-\theta\sigma)/\theta,$$

and comparing this with $F = E-\theta\sigma$ we find

$$\log A = F/\theta,$$

where F is the Helmholtz free energy of the system corresponding to the distribution (20.3). Thus the Gibbs distribution (20.3) can be written in the form

$$\rho = e^{\{F-E(p,q)\}/\theta}, \tag{27.1}$$

which is in fact the form in which it is most often used.

The normalization condition now becomes

$$\int e^{\{F-E(p,q)\}/\theta}\, d\Gamma = 1. \tag{27.2}$$

Since $e^{F/\theta}$ does not depend on the coordinates and momenta of the system, it can be taken outside the integral, and (27.2) becomes

$$e^{-F/\theta} = \int e^{-E(p,q)/\theta}\, d\Gamma. \tag{27.3}$$

Taking logarithms, we obtain the Helmholtz free energy

$$F = -kT\log\int e^{-E(p,q)/\theta}\, d\Gamma. \tag{27.4}$$

This formula can be used to calculate the free energy of any system whatever. We may note that the integral under the logarithm is usually called the *partition function*.

When the system to which (27.4) is to be applied consists of

identical molecules, it is necessary to make an important remark about the integration in (27.4) (and in (27.2) and (27.3)). It is easy to see that if two (or more) molecules of the substance are exchanged, then after the exchange the system will be represented in phase space by a different point, which can be obtained from the original point if the coordinates and momenta of one molecule are replaced by those of the coordinates and momenta of the other. However, since all the molecules are identical, these two states of the substance must be physically indistinguishable. In other words a single physical state of the substance corresponds to a number of different points in phase space. Now the integration in (27.2) should be taken only over all those states which are physically distinguishable, for only in this case does ρ have the multiplicative property. Thus if the integration is extended over the whole of phase space (i.e. over all the states corresponding to different points in phase space), the result must be divided by the number of points in phase space corresponding to a single physical state. This number is clearly the number of permutations of all the N molecules of the substance, i.e. $N!$.

Let us split up $d\Gamma$ (the product of the differentials of all the coordinates and momenta of the body) into the products $d\tau_1, d\tau_2, \ldots, d\tau_N$, where $d\tau_i$ is the product of the differentials of the momenta and coordinates of a single molecule, i.e. the element of phase volume for the ith molecule.

For systems consisting of identical molecules (27.2) must, by the above considerations, be replaced by

$$\int e^{\{F-E(p,q)\}/\theta} \frac{d\tau_1 d\tau_2 \ldots d\tau_N}{N!} = 1. \tag{27.5}$$

Correspondingly, (27.4) now becomes

$$F = -kT \log \frac{1}{N!} \int e^{-E(p,q)/kT} \, d\tau_1 \, d\tau_2 \ldots d\tau_N. \tag{27.6}$$

If the substance were to consist of particles of several different kinds, with N_i particles of type i, this formula would have to be replaced by

$$F = -kT \log \frac{1}{N_1! \, N_2! \ldots} \int e^{-E(p,q)/kT} \, d\tau_1 \, d\tau_2 \ldots d\tau_{N_1+N_2\ldots}.$$

We may remark in conclusion, that by forming the complete differential of the normalization condition (27.2), it is easy to obtain the thermodynamic identity.

28. The perfect gas

We shall now apply (27.6) to a perfect gas; since the interaction energies of the molecules may be neglected, the energy of a perfect gas may be written as the sum of the energies ϵ_i of each of the N molecules

$$E(p,q) = \sum_{i=1}^{N} \epsilon_i, \tag{28.1}$$

where ϵ_i is a function of the coordinates and momenta of the ith molecule:

If (28.1) is substituted into (27.6), the partition function occurring in the latter becomes the product of the partition functions of each of the molecules:

$$\int e^{-E(p,q)/\theta}\, d\tau_1\, d\tau_2 \ldots d\tau_N = \int e^{-\epsilon_1/\theta}\, d\tau_1 \ldots \int e^{-\epsilon_N/\theta}\, d\tau_N.$$

Now since all the molecules are identical, all these integrals are clearly equal to each other, since they differ only in the labelling of the variables of integration (each of the integrations is extended over the whole phase space of the particular molecule). The suffix i in ϵ_i and $d\tau_i$ may therefore be suppressed, giving

$$\int e^{-E(p,q)/\theta}\, d\tau_1 \ldots d\tau_N = \left(\int e^{-\epsilon/\theta}\, d\tau\right)^N,$$

where ϵ and $d\tau$ are the energy and the volume element of phase space for any one of the molecules; (27.6) now becomes

$$F = -kT \log \frac{\left(\int e^{-\epsilon/\theta}\, d\tau\right)^N}{N!} = -NkT \log \int e^{-\epsilon/\theta}\, d\tau + kT \log N!$$

Since N is a very large number (the number of molecules in the gas) Stirling's formula† may be used to evaluate $\log N!$. Combining these terms we finally obtain

$$F = -NkT \log \frac{e}{N} \int e^{-\epsilon/kT}\, d\tau \tag{28.2}$$

for the Helmholtz free energy of a perfect gas made up of identical molecules.

When there is no external field, the energy of a perfect gas molecule is evidently independent of the coordinates of its centre of gravity, i.e. of its position as a whole. Thus the integration in (28.2) over these coordinates may be carried out, and since the integration is to

† For a large number N, the sum of the series $\log N! = \log 1 + \log 2 + \ldots + \log N$ is approximately equal to the integral $\int_1^N \log x\, dx = N(\log N - 1)$. The formula $\log N! = N \log N/e$, which is true for large integers, is known as Stirling's formula.

be extended over all possible values of these coordinates, i.e. over the whole volume of the gas, we obtain simply this volume V. Let $d\tau'$ be the product of the differentials of the momenta and the coordinates of a molecule, with the exception of the coordinates of its centre of gravity, then (28.2) becomes

$$F = -NkT\log\left[\frac{eV}{N}\int e^{-\epsilon/kT}\,d\tau'\right]; \tag{28.3}$$

this very important formula makes possible the evaluation of the Helmholtz free energy, and consequently of all the thermodynamic quantities, for a perfect gas.

The integral in (28.3) cannot be further reduced without some definite assumptions about the properties of a molecule, in particular the dependence of its energy on its coordinates and momenta. It is, however, important to note that it is a function of the temperature only. If we denote $-kT\log\int e^{-\epsilon/kT}\,d\tau'$ by some function of temperature $f(T)$, then (28.3) becomes

$$F = -NkT\log(eV/N)+Nf(T). \tag{28.4}$$

In spite of the presence of an unknown function of temperature several important properties of a perfect gas in the absence of external field may be deduced from this formula.

Thus by (17.10) the gas pressure is

$$p = -\partial F/\partial V = NkT/V,$$

or

$$pV = NkT. \tag{28.5}$$

This relation is well known as the *equation of state of an ideal gas* or as *Clapeyron's equation*. It is usually written as

$$pV = RT, \tag{28.6}$$

where

$$R = Nk \tag{28.7}$$

is called the gas constant.

Knowing F, we can also find the other thermodynamic functions. In particular the Gibbs free energy is

$$G = F+pV = -NkT\log(eV/N)+Nf(T)+pV.$$

Expressing V in terms of p and T by means of (28.5) (G has to be expresssed as a function of p and T) and introducing a new function of temperature $\chi(T) = f(T)-kT\log kT$ we obtain

$$G = NkT\log p+N\chi(T). \tag{28.8}$$

By (17.10) the entropy has the form

$$S = -\partial F/\partial T = Nk\log(eV/N) - Nf'(T), \tag{28.9}$$

or as a function of p and T (by (17.13))

$$S = -\partial G/\partial T = -Nk\log p - N\chi'(T). \tag{28.10}$$

Finally, the energy is

$$E = F + TS = Nf(T) - NTf'(T) \tag{28.11}$$

and is therefore a *function of temperature only* and in particular does not depend on the volume of the gas. The heat function is

$$H = E + pV = Nf(T) - NTf'(T) + pV = Nf(T) - NTf'(T) + NkT \tag{28.12}$$

and is therefore also independent of the volume.

The same is true of the specific heats C_v and C_p, which are also evidently functions of temperature only. Moreover, from (15.6) and (15.7), making use of (28.11) and (28.12), we find

$$C_p - C_v = (\partial H/\partial T)_p - (\partial E/\partial T)_v = Nk = R. \tag{28.13}$$

EXAMPLES

1. Find the work done on an ideal gas and the quantity of heat absorbed by it, in an isothermal change of volume from V_1 to V_2 (or of pressure from p_1 to p_2).

SOLUTION. According to § 17 the work W is equal to the change of Helmholtz free energy and so, by (28.4),

$$W = F_2 - F_1 = NkT\log(V_1/V_2) = NkT\log(p_2/p_1).$$

The quantity of heat is

$$Q = T(S_2 - S_1) = NkT\log(V_2/V_1).$$

The last result also follows immediately from the fact that $W+Q$ is equal to the change of energy, which is zero for an ideal gas in an isothermal process.

2. Find the heat capacity of an infinite vertical column of a monatomic perfect gas in the gravitational field (total number of molecules $= N$, cross-section area of the column $= s$).

SOLUTION. Substituting in (28.2) $\epsilon = p^2/2m + mgz$ for the energy of a gas molecule, where z is the height above sea-level, we have for the Helmholtz free energy of the column,

$$F = -NkT\log[eskT(2\pi mkT)^{\frac{3}{2}}/Nmg].$$

The energy of the gas is

$$E = F - T\partial F/\partial T = \tfrac{5}{2}NkT,$$

and the heat capacity $$C = \tfrac{5}{2}Nk.$$

3. Find the centre of gravity of an infinite column of gas (the same as in Ex. 2).

Solution. Making use of (11.3) we have

$$\frac{\overline{\partial E(p,q)}}{\partial g} = \left(\frac{\partial E}{\partial g}\right)_S = \left(\frac{\partial F}{\partial g}\right)_T,$$

where g is the acceleration of gravity.

Now that part of the energy which depends on g, i.e. the potential energy in the gravitational field, is $mgN\bar{z}$, where $\bar{z}$ is the mean height of a molecule above sea-level, and is obviously also the height of the centre of gravity of the column; thus

$$\partial F/\partial g = \partial E/\partial g = Nm\bar{z},$$

and using the result of Ex. 2 we find

$$\bar{z} = \frac{1}{mN}\frac{\partial F}{\partial g} = \frac{kT}{mg}.$$

4. Two identical gases, with equal temperatures T and equal numbers of particles N, but with different pressures p_1 and p_2 (and volumes V_1 and V_2) are contained in separate vessels. Find the change of entropy when the vessels are connected.

Solution. Before the vessels were connected the total entropy was just the sum of the entropies of the separate gases, or by (28.10)

$$S_0 = -Nk\log p_1 p_2 - 2N\chi'(T).$$

After connexion of the vessels the temperature remains constant (as follows immediately from the conservation of energy of both gases). The pressure is then given by

$$\frac{1}{p} = \frac{V_1+V_2}{2NkT} = \frac{1}{2}\left(\frac{1}{p_1}+\frac{1}{p_2}\right).$$

The entropy is therefore

$$S = 2Nk\log\frac{1}{2}\left(\frac{1}{p_1}+\frac{1}{p_2}\right) - 2N\chi'(T).$$

Thus the change of entropy is

$$\Delta S = Nk\log[(p_1+p_2)^2/4p_1p_2].$$

5. Find the Helmholtz free energy of a perfect gas in a cylindrical vessel of radius R and length h, rotating about its axis with angular velocity Ω.

Solution. As was shown in § 25 the rotation introduces a 'centrifugal energy' $-\frac{1}{2}m\Omega^2r^2$. Applying the general formula (28.2) we find the free energy F' in the rotating system of coordinates

$$F' = F_0 - NkT\log\left[\frac{2}{R^2h}\int\limits_0^R\int\limits_0^h e^{m\Omega^2r^2/2kT}r\,drdz\right]$$

$$= F_0 - NkT\log\left[\frac{2kT}{m\Omega^2R^2}(e^{m\Omega^2R^2/2kT}-1)\right],$$

where F_0 is the Helmholtz free energy of the gas when not rotating.

The angular momentum of the gas is given by

$$M = -\frac{\partial F'}{\partial\Omega} = -\frac{2NkT}{\Omega} + \frac{NmR^2\Omega}{1-e^{-m\Omega^2R^2/2kT}},$$

while the energy in the rotating system of coordinates is

$$E' = F' - T\frac{\partial F'}{\partial T} = E_0 - \frac{Nm\Omega^2R^2}{2(1-e^{-m\Omega^2R^2/2kT})} + NkT,$$

and the energy in the stationary system of coordinates (see 19.4) is

$$E = E' + M\Omega = E_0 + \frac{Nm\Omega^2R^2}{2(1-e^{-m\Omega^2R^2/2kT})} - NkT$$

(E_0 is the energy of the gas when not rotating).

29. A perfect gas not in equilibrium

The previous considerations referred to a perfect gas in a state of statistical equilibrium, and therefore describable by a Gibbs distribution. We may ask what would be the entropy of the gas in some macroscopic state, which is not an equilibrium state. This can be determined if we can find the statistical weight of the state, for then, according to (7.6), its logarithm will give the entropy of the gas in this state.

Any state of an ideal gas can be described in the following way. Let us divide the phase space of a single molecule (all the molecules are supposed identical) into a series of small regions $\Delta\tau_1$, $\Delta\tau_2$... (the indices 1, 2... here refer of course not to different molecules, but to different parts of the same phase space) which are, however, each large enough to contain a large number of molecules. Then the state of the gas can be specified by the values of the number N_i (which is very large) of molecules in the ith region, for all values of i. The total number of molecules is $N = \sum_i N_i$.

The statistical weight $\Delta\Gamma$ of the state (i.e. of the distribution of molecules characterized by the numbers N_i) is the volume occupied by the gas in this state in phase space (i.e. the phase space of the gas as a whole). It can be expressed as $\Delta\Gamma = \prod_i \Delta\Gamma_i$, where $\Delta\Gamma_i$ is the statistical weight for those molecules which are in the ith region $\Delta\tau_i$ of their own phase space. Since there are N_i such molecules, $\Delta\Gamma_i$ should have the value $(\Delta\tau_i)^{N_i}$. However, by considerations analogous to those of § 27, this must be divided by the number of permutations of the N_i molecules among themselves, i.e. by $N_i!$, since such permutations do not change the state of the gas. In this way we find

$$\Delta\Gamma_i = (\Delta\tau_i)^{N_i}/N_i!,$$

and the statistical weight of the state of the whole gas is the product of all the $\Delta\Gamma_i$:

$$\Delta\Gamma = \prod_i [(\Delta\tau_i)^{N_i}/N_i!]. \tag{29.1}$$

We may note here that the statistical method as applied to perfect

gases, with this definition of statistical weight, is known as *Boltzmann's method.*

From the statistical weight it is easy to deduce the entropy

$$\sigma = \log \Delta\Gamma = \sum_i (N_i \log \Delta\tau_i - \log N_i!).$$

If we make use of Stirling's formula (see footnote, p. 69), which is permissible, since N_i is supposed to be sufficiently large, then this equation becomes

$$\sigma = \sum_i N_i \log \frac{e\Delta\tau_i}{N_i}. \tag{29.2}$$

It is more convenient to introduce here instead of N_i, the density n_i of the molecules in the volume $\Delta\tau_i$, so that

$$N_i = n_i \Delta\tau_i.$$

Then (29.2) becomes

$$\sigma = \sum_i n_i \Delta\tau_i \log e/n_i.$$

Since the $\Delta\tau_i$ are small regions, and there is a very large number of them, the summation over the separate regions in this equation may be replaced by an integration over the whole of phase space (of a single molecule):

$$\sigma = \int n \log \frac{e}{n}\, d\tau, \tag{29.3}$$

where n is the density of molecules in phase space ($n\,d\tau$ is the number of molecules in the volume element $d\tau$ of phase space). This formula defines the entropy of an ideal gas in *any* state specified by the distribution of molecules in phase space.

In a state of equilibrium the entropy σ must have a maximum value (the application of this law to a perfect gas is sometimes called *the Boltzmann H theorem*), and from this requirement the distribution of the molecules in a state of statistical equilibrium may be found. To do this we must accordingly find such an n that the integral (29.3) has a maximum, and that satisfies the additional conditions

$$\int n\, d\tau = N, \tag{29.4}$$

$$\int n\epsilon\, d\tau = E, \tag{29.5}$$

which express the fact that the total number of molecules N and the total energy E of the gas are given. Following the well-known Lagrangian method of undetermined coefficients, we must equate to zero the variation of the integral (29.3), after adding the variations

of the integrals (29.4) and (29.5) multiplied by arbitrary constants α and β. We obtain

$$\delta \int n \log \frac{e}{n}\, d\tau + \alpha\delta \int n\, d\tau + \beta\delta \int n\epsilon\, d\tau = 0.$$

Carrying out the variation with respect to the distribution n, we find

$$\int \delta n \left(\log \frac{e}{n} - 1\right) d\tau + \alpha \int \delta n\, d\tau + \beta \int \delta n\epsilon\, d\tau = 0,$$

or

$$\int (-\log n + \alpha + \beta\epsilon)\delta n\, d\tau = 0.$$

Since δn is arbitrary, it is necessary, in order to make this integral identically zero, that

$$-\log n + \alpha + \beta\epsilon = 0,$$

or

$$n = e^{\alpha+\beta\epsilon}.$$

This is nothing else than the already familiar Boltzmann distribution (20.10), the constants α and β being connected with the constant c and the temperature θ in (20.10) by the relations

$$c = e^{\alpha}, \qquad \beta = -1/\theta.$$

Thus we see that the Boltzmann distribution for a gas in statistical equilibrium does indeed satisfy the condition of maximum entropy. It is easy to verify that the maximum value of the entropy (29.3), attained when the gas is in an equilibrium state described by the Boltzmann distribution, just coincides with the value obtained from the free energy (28.2) found in § 28, starting from the Gibbs distribution.

30. Mixtures of perfect gases

The thermodynamic functions E, F, G, H, S are additive quantities, i.e. their values for a group of several systems are equal to the sums of their values for each system separately. This, however, is true only as long as these systems do not interact with each other, or, more precisely, as long as such interactions can be neglected. Thus for mixtures of any two (or more) substances (for instance, of two liquids) the entropy of the mixture will not in general be equal to the sum of the entropies of each separately.

An exception is the mixture of perfect gases, since by definition the interactions of their molecules may be neglected. The entropy, for instance, of such a mixture is the sum of the entropies which each of the components would have if the others were absent, and if this component occupied the volume of the whole mixture, i.e. if it had a

pressure equal to its partial pressure in the mixture. The partial pressure p_i of the ith gas is expressed in terms of the pressure p of the whole mixture by

$$p_i = \frac{N_i kT}{V} = \frac{N_i}{N}p, \tag{30.1}$$

where N is the total number of molecules in the mixture and N_i the number of molecules of the ith gas. Thus by (28.9) the entropy of the mixtures of two gases, for instance, is

$$S = N_1 k \log\frac{eV}{N_1} + N_2 k \log\frac{eV}{N_2} - N_1 f_1'(T) - N_2 f_2'(T), \tag{30.2}$$

or by (28.10) and (30.1)

$$\begin{aligned} S &= -N_1 k \log p_1 - N_2 k \log p_2 - N_1 \chi_1'(T) - N_2 \chi_2'(T) \qquad (30.3) \\ &= -(N_1+N_2)k \log p - N_1 k \log\frac{N_1}{N} - N_2 k \log\frac{N_2}{N} - N_1 \chi_1'(T) - N_2 \chi_2'(T), \end{aligned}$$

while the Helmholtz free energy (by (28.4)) is

$$F = -N_1 kT \log\frac{eV}{N_1} - N_2 kT \log\frac{eV}{N_2} + N_1 f_1(T) + N_2 f_2(T). \tag{30.4}$$

Similarly, the Gibbs free energy (by (28.8) and (30.1)) is

$$\begin{aligned} G &= N_1 kT \log p_1 + N_2 kT \log p_2 + N_1 \chi_1(T) + N_2 \chi_2(T) \qquad (30.5) \\ &= N_1(kT \log p + \chi_1) + N_2(kT \log p + \chi_2) + N_1 kT \log\frac{N_1}{N} + N_2 kT \log\frac{N_2}{N}. \end{aligned}$$

Suppose we have two different gases with N_1 and N_2 molecules respectively, in vessels of volumes V_1 and V_2, at the same temperature and pressure. If the two vessels are now connected so that the gases mix, the volume of the mixture will be V_1+V_2, while its pressure and temperature remain the same. The entropy, however, changes; in fact, before mixing, the entropy of both gases, equal to the sum of their separate entropies, was

$$S_0 = N_1 k \log\frac{eV_1}{N_1} + N_2 k \log\frac{eV_2}{N_2} - N_1 f_1'(T) - N_2 f_2'(T).$$

After mixing, the entropy, according to (30.2), becomes

$$S = N_1 k \log\frac{e}{N_1}(V_1+V_2) + N_2 k \log\frac{e}{N_2}(V_1+V_2) - N_1 f_1'(T) - N_2 f_2'(T),$$

and the change of entropy is therefore

$$\Delta S = S - S_0 = N_1 k \log\frac{V_1+V_2}{V_1} + N_2 k \log\frac{V_1+V_2}{V_2},$$

or, since for the same pressure and temperature the volumes are proportional to the numbers of particles,

$$\Delta S = N_1 k \log(N/N_1) + N_2 k \log(N/N_2). \tag{30.6}$$

This quantity is clearly positive, i.e. the entropy increases on mixing (irreversible process).

If both gases had been identical, the entropy after connecting the vessels would have been

$$S = (N_1+N_2)k \log \frac{e(V_1+V_2)}{(N_1+N_2)} - (N_1+N_2)f'(T),$$

and since $(V_1+V_2)/(N_1+N_2) = V_1/N_1 = V_2/N_2$, (on account of the equality of pressure and temperature in the gases), the change of entropy would evidently have been zero.

Thus the change of entropy on mixing is connected primarily with the difference between the molecules of the constituents. It is important, however, to point out that this difference may be purely formal and need not be connected with a physical difference between the molecules. For instance, the molecules of one gas may be labelled by the number 1, and the molecules of the other gas (of the same kind) by the number 2. Then on mixing the gases the entropy will nevertheless change in spite of the fact that the gases are physically identical. This corresponds to the circumstance that a certain amount of work is necessary to separate out again the molecules labelled 1 from those labelled 2.

31. Deviations from the perfect gas

The preceding discussion is applicable to gases actually occurring in nature only if they are sufficiently dilute. We may remark, however, that the approximation made in considering gases as perfect is quite sufficient in a large number of cases, so that, for instance, Clapeyron's equation (28.5), which strictly speaking applies only to perfect gases, can in practice very often be used.

This approximation may, however, sometimes prove insufficient, and it is then necessary to calculate the deviations of the properties of the actual gas from those of a perfect gas. This is possible if the gas is still dilute enough for collisions between molecules to be relatively rare. In this case, simultaneous collisions of two or more pairs of molecules are clearly very much less probable than the collision of a single pair, and we assume therefore that only one pair of molecules

collides at a time, and calculate the free energy of the gas with this approximation.

To do this we must again start from the general formula (27.6). However, the energy must be taken not as (28.1) but as

$$E(p,q) = \sum_i \epsilon_i + U, \tag{31.1}$$

where ϵ_i is the energy of the ith molecule and U is the interaction energy of the molecules with each other. (27.6) then gives

$$F = -kT \log \frac{1}{N!} \int e^{-(\sum_i \epsilon_i + U)/kT} \, d\tau_1 ... d\tau_N. \tag{31.2}$$

We examine first the case of a monatomic gas. The interaction energy U evidently depends on the distances between atoms, i.e. on their coordinates. We split up each of the $d\tau_i$ into the product of $d\tau_i'$ and dV_i, where dV_i is the product of the differentials of the coordinates of the ith atom ($dV_i = dx_i \, dy_i \, dz_i$) and $d\tau_i'$ is the product of the differentials of its momenta. We can then express the integral in (31.2) as the product of two integrals of $e^{-U/kT}$ and $e^{-\sum_i \epsilon_i/kT}$ with respect to $dV_1 ... dV_N$ and $d\tau_i' ... d\tau_N'$ respectively, and after rearranging (adding $\log V^N$ to the second term and subtracting $\log V^N$ from the first) we obtain

$$F = -kT \log \frac{V^N}{N!} \int e^{-\sum_i \epsilon_i/kT} \, d\tau_1' ... d\tau_N' - kT \log \int e^{-U/kT} \, dV_1 ... dV_N / V^N.$$

It is easily shown that the first term is just the free energy of the perfect gas (28.3), and calling this F_{id} we have

$$F = F_{id} - kT \log \int \frac{e^{-U/kT} \, dV_1 ... dV_N}{V^N}.$$

This can be rewritten in the form

$$F = F_{id} - kT \log \left(\frac{1}{V^N} \int (e^{-U/kT} - 1) \, dV_1 \, dV_2 ... dV_N + 1 \right).$$

Since we assume the gas to be rather dilute, i.e. the volume V rather large, the first term under the logarithm is small compared with unity. We may therefore use the approximation $\log(1+x) \simeq x$ for $x \ll 1$ and we have approximately

$$F = F_{id} - \frac{kT}{V^N} \int (e^{-U/kT} - 1) \, dV_1 ... dV_N . \dagger \tag{31.3}$$

† We shall see below that the first term under the logarithm sign in the previous equation is proportional to N^2/V. Thus at first sight it might seem that in order that this term should be small compared with unity (and consequently that (31.3) should be valid) it would be necessary not only for N/V to be sufficiently small, but also that

We now make use of our assumption that at any instant not more than one pair of atoms collide.

The interaction between atoms is only appreciable when they are very close to each other, i.e. when they actually collide. Thus the integral in (31.3) is only appreciably different from zero when some two atoms are very close to each other. According to our assumption this can only be the case for a single pair of atoms at any one instant, and this pair can be chosen from the N atoms in $\frac{1}{2}N(N-1)$ ways. Thus the integral in (31.3) can be written as

$$\tfrac{1}{2}N(N-1)\int (e^{-U_{12}/kT}-1)\, dV_1 \ldots dV_N,$$

where U_{12} is the interaction energy of two atoms (which two is irrelevant on account of their identity). U_{12} depends only on the coordinates of the two atoms and we may therefore integrate over all the others, giving V^{N-2}. Also $N(N-1)$ may be replaced by N^2, since N is a very large number. Substituting into (31.3) we obtain

$$F = F_{id} - \frac{kTN^2}{2V^2}\int (e^{-U_{12}/kT}-1)\, dV_1\, dV_2,$$

where $dV_1\, dV_2$ is the product of the differentials of the coordinates of any two atoms.

Now U_{12} is evidently a function only of the distance between the two atoms, i.e. of the differences of their coordinates. Thus if we introduce instead of the coordinates of the separate atoms the coordinates of their centre of gravity and their coordinates relative to it, U_{12} will depend only on the latter (the product of whose differentials we denote by dV). We may then integrate over the coordinates of the centre of gravity, giving again the volume V, and we obtain finally

$$F = F_{id} - kTN^2J/2V, \tag{31.4}$$

where

$$J = \int (e^{-U_{12}/kT}-1)\, dV.$$

From this we may obtain the gas pressure as

$$p = -\frac{\partial F}{\partial V} = \frac{NkT}{V} - \frac{kTN^2J}{2V^2} \tag{31.5}$$

since $-\partial F_{id}/\partial V = p_{id} = NkT/V$, by (28.5).

the quantity of gas, i.e. N, should not be very large. However, we shall see later (§ 43) that since F is an additive function, it must always have the form $F = Nf\{T, (N/V)\}$, and so results deduced for a small quantity of gas are automatically valid for any quantity of gas.

In § 17 we mentioned that the changes of free energy δF, δG for a small change of the external conditions or of the properties of the body are equal, the one being taken at constant volume and the other at constant pressure (see (17.17)). If we regard the deviation of a gas from a perfect gas as a change of this kind, then from (31.4) we can immediately obtain G. For this it is only necessary to express the volume in terms of pressure in the correction term of (31.4), and this can be done by Clapeyron's equation, since the second term in (31.5) can be neglected here (it would lead to a correction of higher order of small quantities).

We obtain in this way

$$G = G_{id} - \tfrac{1}{2}NpJ, \tag{31.6}$$

from which the volume can be found as

$$V = (NkT/p) - \tfrac{1}{2}NJ. \tag{31.7}$$

All the above referred to a monatomic gas, but it is easy to show that the same formulae remain valid also for polyatomic gases. In this case the potential energy of interaction of the molecules with each other depends on their relative positions and is a function, for instance, of the coordinates of their centres of gravity and some other coordinates which serve to specify the orientation of the molecules in space (angular coordinates). Thus in $d\tau_i = d\tau_i' dV_i$, the dV_i must contain the differentials of all these coordinates and the $d\tau_i'$ all the remaining coordinates and all the momenta. However, the angular coordinates may be chosen in such a way that the integral $\int dV_i$ is equal to the volume V of the gas. In fact, integration over the coordinates of the centre of gravity gives this volume V, while integration over the angles always gives some constant which can be made unity by suitable normalization of the angular coordinates. Thus all the formulae deduced in this paragraph retain the same form also for polyatomic gases, with the only difference that in (31.4–7) dV is now the product of the differentials of the coordinates specifying not only the relative distance between two molecules but also their relative orientation.

32. Van der Waals' equation

In gases the interaction between molecules is extremely small. As this interaction is increased the properties of the gas depart more and more from those of a perfect gas, and the gas goes over continu-

ously into a condensed system, i.e. a liquid. In the latter the molecular interaction is large and the properties of this interaction (and therefore of the liquid), i.e. the form of the potential energy of interaction of all the molecules as a function of all their coordinates, depends very much on the actual nature of the liquid. For this reason it is not possible to establish any general formulae giving a quantitative description of the properties of liquids.

It is, however, possible to find an *interpolation formula* which describes qualitatively the transition from liquid to gas. This formula has to yield correct results in two limiting cases. At large volumes and high temperatures, i.e. for dilute gases, it must go over into the perfect gas formula, while for small volumes and low temperatures, when the gas approaches the liquid state, it must reproduce the limited compressibility of fluids. Such a formula will then describe qualitatively the behaviour of the gas for intermediate conditions also.

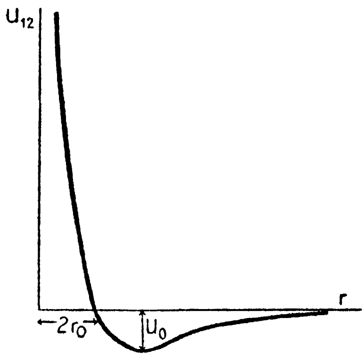


FIG. 3.

In order to deduce a formula of this kind we investigate in greater detail the deviations from a perfect gas in the region of high temperatures, when the gas is almost perfect. As in § 31, we shall first of all examine the case of a monatomic gas, and by just the same considerations as there, all the formulae obtained in this way will apply also to polyatomic gases.

The only assumption made in § 31 about the potential energy of interaction of two molecules of a gas, i.e. about the function U_{12}, was that this function diminished rapidly with distance. Actually, however, it is known that the function U_{12} for a monatomic gas has a form like that shown in Fig. 3, where the abscissae represent the distance separating the atoms. For small distances U_{12} grows with decrease of distance, corresponding to repulsive forces between the atoms. At some distance $(2r_0)$, U_{12} changes sign and begins to grow very large, corresponding to the non-interpenetrability of atoms, i.e. the practical impossibility of approach closer than a certain distance (for this reason r_0 is sometimes called the 'radius'

of the atom). At large distances U_{12} slowly increases with increase of r, and asymptotically approaches zero, this increase of U_{12} corresponding to an attractive force between the atoms. The minimum of U_{12}, i.e. the point where $\partial U_{12}/\partial r$ becomes zero, represents a position of stable equilibrium. At this point the absolute value U_0 of the energy, for the high temperatures with which we shall be concerned here, is much smaller than kT, i.e.

$$U_0 \ll kT. \tag{32.1}$$

In the case of a polyatomic gas the interaction energy has a similar character, although of course it cannot be represented in the form of a curve such as Fig. 3, since it is a function of a larger number of variables (including, in particular, the angular coordinates).

This information about the form of the function U_{12} is sufficient for finding the temperature dependence of the integral in (31.4). Since U_{12} depends only on the distance r between the atoms, we may write instead of dV the element of volume which corresponds to a distance between atoms in the interval dr, i.e. $4\pi r^2\,dr$. The integration over dr is extended, of course, over all values of r, i.e. from 0 to ∞. Dividing the range of integration into two parts we may write

$$\int_0^\infty (e^{-U_{12}/kT}-1)\,dV = \int_0^{2r_0} 4\pi(e^{-U_{12}/kT}-1)r^2\,dr + \int_{2r_0}^\infty 4\pi(e^{-U_{12}/kT}-1)r^2\,dr.$$

Now for values of r between 0 and $2r_0$ the potential energy U_{12} is on the whole very large, and so $e^{-U_{12}/kT}$ may, in the first integral, be neglected in comparison with unity. This integral then has the value $-2b$, where

$$b = \frac{16}{3}\pi r_0^3. \tag{32.2}$$

If we consider r_0 as the 'radius' of the atom, then b is clearly four times the 'volume' of the atom (for polyatomic gases this constant is of course not equal to four times the volume of the molecule).

In the second integral U_{12} is nowhere of greater absolute value than U_0 (see Fig. 3), so $-U_{12}/kT$ is always small compared with unity, since even when $U_{12} = -U_0$, $U_0/kT \ll 1$, according to (32.1). Thus $e^{-U_{12}/kT}$ may be expanded in powers of U_{12}/kT, and only the first two terms need be considered. This integral then becomes

$$-\frac{1}{kT}\int_{2r_0}^\infty 4\pi U_{12} r^2\,dr.$$

Since in the whole range of integration U_{12} is negative, this quantity must be positive and we write it as $2a/kT$, where a is a positive constant.

In this way we have found that

$$\int (e^{-U_{12}/kT}-1)\,dV = -2b+2a/kT.$$

Substituting into (31.4) and (31.6) we find for the free energies of the gas

$$F = F_{id}+N^2(kTb-a)/V, \tag{32.3}$$

$$G = G_{id}+Np(b-a/kT). \tag{32.4}$$

The desired interpolation formula, i.e. one which gives correct results at the extremes of some range of values (in this case the range of values of the volumes), may be obtained from (32.3), which does not itself satisfy this requirement (since it does not give the limited compressibility of the gas). For this purpose we substitute in (32.3) the expression

$$F_{id} = -NkT\log(eV/N)+Nf(T),$$

(see (28.4)), and we then obtain

$$F = Nf(T)-NkT\log(eV/N)-NkT\left(\log V-\frac{Nb}{V}\right)-\frac{N^2a}{V}. \tag{32.5}$$

In the deduction of the formulae (31.4) and (32.3) for the Helmholtz free energy we assumed that the gas, although not so dilute as to be considered perfect, had, however, a rather large volume (in particular, so large that we could neglect the possibility of simultaneous collisions of more than two molecules); consequently the distance between molecules is in general considerably larger than their sizes. Thus, in any case, the volume V of the gas is considerably larger than Nb, which from (32.2) is four times the 'volume' of the molecules, i.e. $Nb/V \ll 1$, and making use of the approximation $\log(1+x) \simeq x$ for $x \ll 1$ we have

$$\log(V-Nb) = \log V-\frac{Nb}{V}.$$

Consequently (32.5) can be written as

$$F = Nf(T)-NkT\log e(V/N-b)-N^2a/V. \tag{32.6}$$

In this form the Helmholtz free energy satisfies the requirement mentioned above, that for large V it goes over into the Helmholtz free energy of a perfect gas. At the same time it shows the impossibility

of unlimited compressibility of the gas, since for $V < Nb$ the argument of the logarithm becomes negative.

Knowing the free energy, we can deduce the pressure of the gas

$$p = -\frac{\partial F}{\partial V} = \frac{NkT}{V-Nb} - \frac{N^2a}{V^2},$$

or

$$\left(p+\frac{N^2a}{V^2}\right)(V-Nb) = NkT = RT. \tag{32.7}$$

This is known as *van der Waals' equation*. It is, of course, only one of an infinite number of possible interpolation formulae satisfying the requirements discussed above, and there is no physical reason for choosing any particular one; van der Waals' equation is, however, the simplest of them, and consequently the most convenient.

EXAMPLES

1. Find $C_p - C_v$ for a gas satisfying van der Waals' equation.

SOLUTION. From the result of Ex. 11, § 18, we have

$$C_p - C_v = -T\left(\frac{\partial p}{\partial T}\right)_V^2 \Big/ \left(\frac{\partial p}{\partial V}\right)_T.$$

Substituting for p from van der Waals' equation we find

$$C_p - C_v = Nk\Big/\left[1-\frac{2Na}{kTV^3}(V-Nb)^2\right].$$

2. Find the variation of temperature with pressure in the Joule-Thomson effect for a non-perfect gas which has the Gibbs free energy (32.4).

SOLUTION. The required variation is given by $(\partial T/\partial p)_H$. From the result of Ex. 16, § 18,

$$\left(\frac{\partial T}{\partial p}\right)_H = \left[T\left(\frac{\partial V}{\partial T}\right)_p - V\right]\Big/C_p.$$

From (32.4) we have

$$V = \frac{\partial G}{\partial p} = \frac{NkT}{p} + N\left(b-\frac{a}{kT}\right)$$

(since $\partial G_{id}/\partial p = V_{id} = NkT/p$). Substituting, we find

$$\left(\frac{\partial T}{\partial p}\right)_H = \left[\frac{2Na}{kT} - Nb\right]\Big/C_p.$$

33. The equipartition law

Equation (28.3) defines the Helmholtz free energy of a perfect gas (in the absence of an external field), and in the deduction of this equation no assumption was made as to the behaviour of the atoms within the molecules, if the gas was polyatomic. Owing to this, it was, in particular, not possible to obtain the temperature dependence of the free energy.

A molecule is a configuration of atoms in stable equilibrium, corresponding to a minimum of potential energy. The atoms within a molecule are not, however, fixed and can in fact move, departing from their equilibrium positions. Now in order that the molecule should nevertheless be stable, it is necessary that the energy of motion of the atoms within a molecule should be small compared with the binding energy of the molecule. For this reason the atoms can execute only quite small oscillations about their equilibrium positions. The potential energy of interaction of the atoms with each other is, as is well known from the theory of small oscillations,

$$u = u_0 + \sum_{i=1}^{m} \sum_{k=1}^{m} a_{ik} q_i q_k,$$

where u_0 is the potential energy corresponding to the equilibrium positions; the second term is a quadratic function of the coordinates q_i which specify the departures of the atoms from these positions. The number m of these coordinates is equal to the number of degrees of freedom of oscillation of the molecule.

The number m can be deduced from the number n of atoms in the molecule. The molecule has in fact $3n$ degrees of freedom of which three correspond to the progressive motion of the molecule as a whole and three to its rotation as a whole. If all the atoms are disposed along a single straight line (in particular for a diatomic molecule), then there are only two degrees of rotational freedom, corresponding to the fact that the straight line cannot rotate about itself. The remaining $(3n-6)$ (or $(3n-5)$) degrees of freedom correspond to oscillations of the atoms within the molecule. For monatomic molecules ($n = 1$) there are, of course, no vibrational degrees of freedom, since all three degrees of freedom correspond to progressive motion ($m = 0$) (u_0 is, of course, also zero in this case).

The total energy ϵ of a molecule is the sum of the potential energy u and the kinetic energy. The latter is a quadratic function of all the momenta of the molecule, the number of which is equal to the total number of degrees of freedom (i.e. progressive, rotational, and vibrational) of the molecule, i.e. $3n$. Thus the energy ϵ has the form

$$\epsilon = u_0 + f_{\text{II}}(p, q),$$

where $f_{\text{II}}(p, q)$ is some quadratic function of the momenta and coordinates of the molecule. The total number of variables (i.e. momenta and coordinates) in this function is $r = 6n-6$ (or $(6n-5)$), of which

$3n$ are momenta and $3n-6$ (or $(3n-5)$) coordinates. If $n = 1$, i.e. for a monatomic molecule, then $r = 3$, since the coordinates do not enter at all into the energy.

Substituting this expression for the energy into (28.3) we obtain

$$F = -NkT\log\left[\frac{eVe^{-u_0/kT}}{N}\int e^{-f_{\text{II}}(p,q)/kT}\,d\tau'\right].$$

To find the temperature dependence of the integral in this formula we introduce new variables $p_1', p_2',...; q_1', q_2',...$ instead of $p_1, p_2,...; q_1, q_2,...$, defined by

$$q_i = q_i'\sqrt{T}, \qquad p_i = p_i'\sqrt{T}.$$

Since $f_{\text{II}}(p,q)$ is a quadratic function of coordinates and momenta,

$$f_{\text{II}}(p,q) = Tf_{\text{II}}(p',q'),$$

and this removes T from the exponent. Moreover, when we substitute these new variables in $d\tau'$, we obtain a factor $T^{\frac{1}{2}r}$ since we change only r of the variables (those which enter in the energy), and this factor can be taken outside the integral. The integration over the coordinates q_i is taken over the range of values which they can assume in the course of the vibrations of the atoms within the molecules. Since, however, the integrand diminishes very rapidly with increase of q_i, the integration can be extended over the whole range $-\infty$ to $+\infty$ as for the momenta. This change of variables does not then affect the limits of integration, and the whole integral will be some constant C, independent of temperature. We obtain in this way

$$F = -NkT\log[eVe^{-u_0/kT}CT^{\frac{1}{2}r}/N],$$

or
$$F = -NkT\log(eV/N) - \tfrac{1}{2}NkTr\log T + Nu_0 + N\alpha T, \tag{33.1}$$

where we have put $\alpha = -k\log C$.

From this we can find the energy of the gas by means of (17.11):

$$E = Nu_0 + \tfrac{1}{2}rNkT = Nu_0 + Nc_v T, \tag{33.2}$$

where c_v is evidently the specific heat per molecule, given by

$$c_v = \tfrac{1}{2}rk. \tag{33.3}$$

It should be noticed that the specific heat C_v ($= Nc_v$) does not depend on temperature, and the same is evidently true of C_p ($= Nc_p$), since by (28.13)

$$c_p = c_v + k = \tfrac{1}{2}(r+2)k. \tag{33.4}$$

(33.1) may accordingly be written as

$$F = Nu_0 - NkT\log(eV/N) - Nc_v T\log T + \alpha TN. \tag{33.5}$$

Adding $pV = NkT$ to this expression we obtain the Gibbs free energy G, after expressing V in terms of pressure and temperature:

$$G = Nu_0 + NkT\log p - Nc_p T\log T + \beta TN, \tag{33.6}$$

where the constant β is given by $\beta = \alpha - k\log k$.

From (33.5) and (33.6) the entropy can be deduced, expressed either in terms of V, T or p, T:

$$S = -\frac{\partial F}{\partial T} = Nk\log\frac{eV}{N} + Nc_v\log T + \eta N \tag{33.7}$$

and

$$S = -\frac{\partial G}{\partial T} = -Nk\log p + Nc_p\log T + \zeta N, \tag{33.8}$$

where η and ζ are constants given by

$$\eta = -\alpha + c_v \quad \text{and} \quad \zeta = -\beta + c_p.$$

We can also obtain the heat function H for a perfect gas; making use of Clapeyron's equation and (33.2) we find

$$H = E + pV = Nc_v T + NkT + NU_0 = Nc_p T + Nu_0. \tag{33.9}$$

Equation (33.2) shows that if we leave the constant u_0 out of account (and it is in fact zero for monatomic gases), the energy of the molecules of an ideal gas is $\frac{1}{2}kT$ multiplied by the number of variables entering into the energy of a single molecule. This may be formulated by saying that an *equal amount* $\frac{1}{2}kT$ *of energy corresponds to each variable entering in the energy expression* (*law of equipartition*).

We must, however, bear in mind that this law has in reality only a limited application, particularly in the region of low temperatures (how low depends on the particular kind of gas). In fact, owing to the fact that the gas in reality obeys quantum and not classical mechanics, the energy and specific heat do not always have the values given by (33.2) and (33.3), but are actually smaller (the deviations from the properties predicted by classical statistics are practically negligible at sufficiently high temperatures, but are large at low temperatures). These differences occur as if with reduction of temperature the number r decreases, first of all corresponding to the vanishing of the vibrational degrees of freedom, and then at much lower temperature to the vanishing of rotational degrees of freedom (this is a particular case of the fact that classical mechanics becomes less and less applicable to motion, the higher the frequency). In these circumstances the number r loses its significance as the number of variables in the energy, and retains its meaning only as a kind of

'effective number of variables', which is the coefficient of proportionality between the energy and $\frac{1}{2}kT$, and need no longer be confined to integral values. The specific heat thus becomes temperature-dependent, so that (33.4) (and all the subsequent formulae) lose their significance of describing the temperature dependence of the free energy. The formulae deduced above apply best of all to monatomic gases, and somewhat worse for diatomic gases; for polyatomic gases their application is, generally speaking, very limited.

When the equipartition law applies, it is easy to find the general form of the probability distribution for the energy of the molecules of the gas. Let $\epsilon' = \epsilon - u_0 = f_{\text{II}}(p,q)$ and consider the volume τ of phase space corresponding to states in which the energy ϵ' is less than or equal to some given value. This volume is then given by $\tau = \int d\tau$, the integration being extended over the region for which $f_{\text{II}}(p,q) \leqslant \epsilon'$. Instead of the r quantities p_i, q_i on which ϵ depends let us introduce new variables $q_i' = q_i/\sqrt{\epsilon'}$, $p_i' = p_i/\sqrt{\epsilon'}$, then the condition $f_{\text{II}}(p,q) \leqslant \epsilon'$ becomes

$$f_{\text{II}}(p',q') \leqslant 1$$

and $\int d\tau$ becomes $\epsilon'^{\frac{1}{2}r} \int d\tau'$; thus since $\int\limits_{f_{\text{II}} \leqslant 1} d\tau'$ is evidently independent of ϵ', we have $\tau = \text{const.}\, \epsilon'^{\frac{1}{2}r}$ and

$$d\tau = \text{const.}\, \epsilon'^{\frac{1}{2}r-1}\, d\epsilon'.$$

Hence the probability distribution with respect to energy is

$$dw_{\epsilon'} = Ae^{-\epsilon'/kT}\epsilon'^{\frac{1}{2}r-1}\, d\epsilon'.$$

The constant A is determined by the normalization condition and we obtain finally

$$dw_{\epsilon'} = \frac{1}{(kT)^{\frac{1}{2}r}\Gamma(\frac{1}{2}r)} e^{-\epsilon'/kT}\epsilon'^{\frac{1}{2}r-1}\, d\epsilon'. \tag{33.10}$$

EXAMPLES

1. Find C_v for a monatomic perfect gas, the energy of whose molecules can be expressed in terms of the momentum by $\epsilon = ap$.

SOLUTION. From (28.3) we have for the Helmholtz free energy:

$$F = -NkT \log \frac{eV}{N} \iiint e^{-ap/kT}\, dp_x\, dp_y\, dp_z.$$

Since the integrand depends only on the absolute values of momentum we may write the 'volume element' in 'momentum space' as $4\pi p^2 dp$ instead of $dp_x dp_y dp_z$. In this way

$$F = -NkT \log \frac{4\pi eV}{N} \int\limits_0^\infty e^{-ap/kT} p^2\, dp.$$

Substituting $p = p'T$ it is easy to show that the integral is proportional to T^3, so that

$$F = -NkT\log(CVT^3/N),$$

where C is a constant, and therefore

$$E = -T^2\frac{\partial}{\partial T}\left(\frac{F}{T}\right) = 3NkT$$

and the specific heat is

$$C_v = 3Nk.$$

2. Find the relation between volume, temperature, and pressure for a perfect gas during an adiabatic process (in this and all the following examples it is to be assumed that the gas obeys the equipartition law).

Solution. Since the entropy remains constant in an adiabatic process, we obtain from (33.8)

$$-Nk\log p + C_p\log T = \text{const.}$$

or

$$T^{C_p}p^{-Nk} = \text{const.}$$

Making use of (28.13) and introducing the quantity

$$\gamma = C_p/C_v$$

we find $T^\gamma p^{1-\gamma} = \text{const.}$, and making use of Clapeyron's equation we find also

$$TV^{\gamma-1} = \text{const.} \quad \text{and} \quad pV^\gamma = \text{const.}$$

3. Two identical perfect gases with equal pressures p and numbers of molecules N, but at different temperatures T_1 and T_2 are contained in vessels of volumes V_1 and V_2. Find the entropy change when the vessels are connected.

Solution. Before the vessels were connected the entropy of the gases together (equal to the sum of their separate entropies) was by (33.8)

$$S_0 = -2Nk\log p + Nc_p\log T_1T_2 + 2\zeta N.$$

After connexion of the vessels, the temperatures of the two gases equalize, the sum of the energies of both gases remaining constant. Using the expression (33.2) for the energy, this can be expressed by

$$c_vT_1 + c_vT_2 = 2c_vT$$

(T being the final common temperature), or $T = \frac{1}{2}(T_1+T_2)$. After connexion of the vessels the total number of particles is $2N$ and occupies a volume $V_1+V_2 = Nk(T_1+T_2)/p$. Thus the pressure is now $2NkT/(V_1+V_2) = p$, i.e. the same as before; the entropy is now

$$S = -2Nk\log p + 2Nc_p\log\tfrac{1}{2}(T_1+T_2) + 2\zeta N$$

and the entropy change

$$\Delta S = S - S_0 = Nc_p\log\frac{(T_1+T_2)^2}{4T_1T_2}.$$

4. Find the work W and quantity of heat Q absorbed by a perfect gas in an adiabatic process.

Solution. By the formula $dQ = TdS$

$$Q = 0 \quad \text{and} \quad W = E_2 - E_1,$$

where $E_2 - E_1$ is the change of energy in the process. Hence from (33.2) we find

$$W = Nc_v(T_2 - T_1),$$

where T_1 and T_2 are the temperatures before and after the process.

W may be expressed in terms of the initial and final volumes V_1 and V_2 using the result of Ex. 2, that

$$V_1^{\gamma-1}T_1 = V_2^{\gamma-1}T_2.$$

Thus
$$W = Nc_v T_1\left[\left(\frac{V_1}{V_2}\right)^{\gamma-1} - 1\right] = Nc_v T_2\left[1 - \left(\frac{V_2}{V_1}\right)^{\gamma-1}\right].$$

5. The same as Ex. 4, but the process now taking place at constant volume (isochorically), instead of adiabatically.

SOLUTION. Since $dW = -p\,dV$,

$$W = 0, \qquad Q = E_2 - E_1 = Nc_v(T_2 - T_1).$$

6. The same as Ex. 4, but at constant pressure (isobaric process).

SOLUTION. Using (33.9) and (28.5) we find

$$W = -p(V_2 - V_1) = Nk(T_1 - T_2), \qquad Q = H_2 - H_1 = Nc_p(T_2 - T_1).$$

7. Find the work done on a gas, and the quantity of heat absorbed by it in a compression of the volume from V_1 to V_2 in accordance with the law $pV^n = a$ (polytropic process).

SOLUTION. The amount of work is

$$W = -\int_{V_1}^{V_2} p\,dV = -\int_{V_1}^{V_2} \frac{a}{V^n}\,dV = \frac{a}{n-1}(V_2^{1-n} - V_1^{1-n}).$$

Since the sum of the quantity of heat and the work is equal to the total change of energy,

$$Q = E_2 - E_1 - W = Nc_v(T_2 - T_1) - W.$$

To find T_2 and T_1 we observe that

$$T = \frac{pV}{Nk} = \frac{a}{Nk}V^{1-n}.$$

Hence we obtain finally

$$Q = \left(\frac{c_v a}{k} + \frac{a}{1-n}\right)(V_2^{1-n} - V_1^{1-n}).$$

8. Find the work done on a perfect gas, and the quantity of heat absorbed by it, in a cyclic process (i.e. when the gas returns to its initial state after the process) consisting of two isochoric and two isobaric processes (i.e. the gas passes from the state p_1, V_1 to p_1, V_2, then to p_2, V_2, then to p_2, V_1, and finally back to p_1, V_1).

SOLUTION. The change of energy in a cyclic process is zero since the final state is the same as the initial one. Thus the work and quantity of heat obtained in such a process are equal and opposite to each other ($W = -Q$). To find W in this case, we observe that no work is done in the isochoric changes, while in the two isobaric processes the work is $-p_1(V_2 - V_1)$ and $-p_2(V_1 - V_2)$. Thus

$$W = (V_2 - V_1)(p_2 - p_1).$$

9. The same as Ex. 8, but for a cyclic process consisting of two isochores and two isotherms (the state of the gas undergoes the following successive changes: (1) V_1, T_1; (2) V_1, T_2; (3) V_2, T_2; (4) V_2, T_1; (5) V_1, T_1).

SOLUTION.
$$W = (T_2 - T_1)Nk\log(V_1/V_2).$$

10. The same as Ex. 8, for a cycle of two isotherms and two adiabatics (the successive states being specified by the following entropies, temperature, and pressures: (1) S_1, T_1, p_1; (2) S_1, T_2; (3) S_2, T_2, p_2; (4) S_2, T_1; (5) S_1, T_1, p_1).

SOLUTION. The quantity of heat absorbed is

$$Q = (T_2 - T_1)(S_2 - S_1).$$

Using (33.8) we find

$$Q = (T_2 - T_1)\{Nk\log(p_1/p_2) + Nc_p\log(T_2/T_1)\}.$$

11. The same as Ex. 8, for a cycle of two isobars and two isotherms (the states being: (1) p_1, T_1; (2) p_1, T_2; (3) p_2, T_2; (4) p_2, T_1; (5) p_1, T_1).

SOLUTION. The work done on the gas in the isobaric processes is $Nk(T_1 - T_2)$ and $Nk(T_2 - T_1)$ (see Ex. 6) and in the isothermal processes (see Ex. 1, § 28) $NkT_2\log(p_2/p_1)$ and $NkT_1\log(p_1/p_2)$. The total work is therefore

$$W = Nk(T_2 - T_1)\log(p_2/p_1).$$

12. The same as Ex. 8, for a cycle of two isobars and two isotherms (the states being: (1) p_1, S_1, T_1; (2) p_1, S_2; (3) p_2, S_2, T_2; (4) p_2, S_1; (5) p_1, S_1, T_1).

SOLUTION. The temperature in the second state is $T_2(p_2/p_1)^{(1-\gamma)/\gamma}$ and in the fourth $T_1(p_1/p_2)^{(1-\gamma)/\gamma}$ (they are found from T_1 and T_2 using the result of Ex. 2). The quantities of heat absorbed by the gas in the adiabatic processes are zero, and in the isobaric processes (see Ex. 6)

$$Nc_p[T_2(p_2/p_1)^{(1-\gamma)/\gamma} - T_1] \quad \text{and} \quad Nc_p[T_1(p_1/p_2)^{(1-\gamma)/\gamma} - T_2],$$

so

$$Q = Nc_pT_1[(p_1/p_2)^{(1-\gamma)/\gamma} - 1] + Nc_pT_2[(p_2/p_1)^{(1-\gamma)/\gamma} - 1].$$

13. The same as Ex. 8, for a cycle of two isochores and two adiabatics (the states being (1) V_1, S_1, T_1; (2) V_1, S_2; (3) V_2, S_2, T_2; (4) V_2, S_1; (5) V_1, S_1, T_1).

SOLUTION. With the help of the result of Ex. 4 we find

$$W = Nc_vT_2[1 - (V_2/V_1)^{\gamma-1}] + Nc_vT_1[1 - (V_1/V_2)^{\gamma-1}].$$

14. Find the maximum amount of work which can be obtained from two identical perfect gases (in separate vessels) having equal temperatures T_0 and equal numbers of particles N but different volumes V_1 and V_2 (and pressures p_1 and p_2), when the vessels are connected.

SOLUTION. In § 14 it was shown that the maximum work is obtained when the process takes place reversibly, i.e. at constant entropy; the work is then equal to the difference of energy before and after the process. Before connexion of the vessels, the entropy of both gases, equal to the sum of their separate entropies, was by (33.7)

$$S_0 = Nk\log e^2\frac{V_1V_2}{N^2} + 2Nc_v\log T + 2\eta N.$$

After connexion of the vessels, we have a gas with $2N$ molecules occupying a volume $V_1 + V_2$ at some temperature T. Its entropy is

$$S = 2Nk\log e\frac{(V_1+V_2)}{2N} + 2Nc_v\log T + 2\eta N.$$

In order that $S_0 = S$ the final temperature has to be

$$T = T_0\left(\frac{4V_1V_2}{(V_1+V_2)^2}\right)^{k/2c_v}.$$

The total energy of both gases before connexion was $E_0 = 2Nc_v T_0 + 2Nu_0$ (by (33.2)). After connexion of the vessels, $E = 2Nc_v T + 2Nu_0$. Thus the maximum work obtainable is

$$W_{\max} = E_0 - E = -2Nc_v T_0\left\{\left(\frac{4V_1V_2}{(V_1+V_2)^2}\right)^{k/2c_v} - 1\right\} = -2Nc_v T_0\left\{\left(\frac{4p_1p_2}{(p_1+p_2)^2}\right)^{k/2c_v} - 1\right\}.$$

15. The same as in the previous example, but with the gases at the same pressure p_0, and different temperatures T_1 and T_2 before connexion.

Solution. Following a method similar to that used in Ex. 14 we find

$$W_{\max} = E_0 - E = Nc_v\left\{T_1 + T_2 - 2\left[\frac{(T_1T_2)^{\frac{1}{2}\gamma}}{\{\frac{1}{2}(T_1+T_2)\}^{\gamma-1}}\right]\right\}.$$

16. A gas escapes adiabatically from a vessel (where it has pressure p_1 and temperature T_1) through a small hole into the exterior where the pressure is p_2. Find the speed of escape.

Solution. Since the hole is small, the flow can be considered as stationary. As the gas is at the same time thermally isolated the condition (16.3) is applicable. For the same reason the speed of the gas inside the vessel can be neglected. (16.3) gives

$$T_1 c_p = \tfrac{1}{2}mv^2 + T_2 c_p,$$

since the heat function of the gas is given by (33.9) (v is the speed of escape, m is the mass of a molecule of the gas). The condition of adiabatic flow (see Ex. 2) gives

$$T_1 p_1^{(1-\gamma)/\gamma} = T_2 p_2^{(1-\gamma)/\gamma}$$

(T_2 is the temperature of the gas after its escape). From these two equations we obtain

$$v^2 = \frac{2c_p T_1}{m}[1-(p_1/p_2)^{(1-\gamma)/\gamma}].$$

17. A stationary stream of gas flows through a tube. At the place where the tube has cross-section s_1 the gas has velocity v_1, temperature T_1, and pressure p_1. Find the velocity v_2 where the cross-section is s_2.

Solution. The condition (16.3) for stationary and adiabatic flow gives similarly to the last example

$$c_p T_1 + \tfrac{1}{2}mv_1^2 = c_p T_2 + \tfrac{1}{2}mv_2^2$$

(p_2, T_2 are pressure and temperature at the place of cross-section area s_2). The adiabatic condition gives

$$T_1 p_1^{(1-\gamma)/\gamma} = T_2 p_2^{(1-\gamma)/\gamma}.$$

The number of particles per unit time crossing the section s_2 must be equal to the number of particles crossing s_1. Bearing in mind Clapeyron's equation, this condition may be written as

$$v_1 s_1 p_1/T_1 = v_2 s_2 p_2/T_2.$$

Substituting p_2 from the third equation into the second, and T_2 from the second into the first, we find for the speed v_2 the equation

$$\tfrac{1}{2}mv_2^2 - \tfrac{1}{2}mv_1^2 = c_p T_1[1-(v_2 s_2/v_1 s_1)^{1-\gamma}].$$

18. Find the equation for an adiabatic process with a gas obeying the equipartition law, but departing from a perfect gas.

SOLUTION. In (32.5) we must now, by (33.5), substitute for $f(T)$

$$f(T) = u_0 - c_v T \log T + \alpha T.$$

Differentiating F with respect to T and collecting constants, we find

$$c_v \log T + k \log(V - Nb) = \text{const.}$$

so that

$$T(V - Nb)^{\gamma-1} = \text{const.}$$

19. Find the change of temperature of a gas (with the properties of Ex. 18) when expanded into a vacuum from volume V_1 to V_2.

SOLUTION. During an expansion into a vacuum the energy of the gas remains constant. Using the expression for $\phi(T)$ in the last example and the expression (32.5) for F, we find

$$E = F - T\,\partial F/\partial T = Nc_v T - Na^2/V + Nu_0.$$

If T_1 and T_2 are the temperature before and after expansion, then the condition $E_1 = E_2$ gives

$$T_2 - T_1 = \frac{Na}{c_v}\left(\frac{1}{V_2} - \frac{1}{V_1}\right).$$

34. Solids

As we have already pointed out, with increase of interaction between the molecules, the gas goes over continuously into a condensed system—a liquid. With further increase of the interaction, we obtain a *solid*, by which we mean a system in which *the atoms execute only small oscillations about equilibrium positions*. The application of statistics to such a system leads again to a number of results. It should be noticed that in order that a body should be solid, its temperature must be sufficiently low (so that kT should be small compared with the potential energy of interaction of the atoms).

In order to determine all the thermodynamic functions of a solid it is necessary as usual to determine the Helmholtz free energy. We shall not at first find the dependence of the free energy on the volume, but only its temperature dependence.

To do this we set out from the general formula (27.6). It is easy, however, to see that in the case of a solid, the left-hand side of (27.5) must be multiplied by $N!$, and so $N!$ will not occur in (27.6), which has the form

$$F = -kT \log \int e^{-E(p,q)/\theta}\, d\tau_1 \ldots d\tau_N. \tag{34.1}$$

The reason for this is that we must take account of the fact that each of the N atoms can carry out its oscillations round any one of N positions of equilibrium in the solid, so that there are $N!$ possible arrangements of the atoms. If the solid consists of molecules which

contain different atoms it is easily seen that (34.1) is still valid. In fact in this case we should have in (27.5), instead of $N!$, the product of the factorials of the numbers of atoms of each kind, but we should have to multiply by the same factor.

Since the atoms of a solid carry out small oscillations about their equilibrium positions (the atoms within a molecule vibrate independently, of course), the energy of the system has the form (similarly to that of the energy of the molecules of a gas)

$$E = Nu_0 + f_{\mathrm{II}}(p, q),$$

where Nu_0 is the interaction energy of the atoms of the whole solid when they are all in their equilibrium positions, N is the number of molecules in the body, and $f_{\mathrm{II}}(p, q)$ is a quadratic function of the momenta and coordinates of all the atoms, and is the sum of the kinetic energy and that part of the potential energy which depends on the coordinates (q_1, q_2... are here the coordinates, specifying the departures of the atoms from their equilibrium positions). The total number of variables in this function is $6nN-6$ (n is the number of atoms per molecule) since it contains all the momenta (whose number equals the number of degrees of freedom of all the atoms, i.e. $3nN$), and also all the coordinates with the exception of three which specify the progressive motion and of three which specify the rotational motion of the body as a whole, i.e. all the vibrational coordinates ($(3nN-6)$ in number). However, in view of the great size of the number nN, we may neglect the 6 in comparison with $6nN$, and say that there are $6nN$ variables in the energy.

Quite similarly to what was found in § 33 for the molecules of a perfect gas, we can show that the integral in (34.1) is equal to some temperature independent quantity a, multiplied by $(\sqrt{T})^{6nN} = T^{3nN}$. Thus

$$F = -kT \log e^{Nu_0/kT} a T^{3nN},$$

or

$$F = Nu_0 - 3nNkT \log T + N\alpha T, \tag{34.2}$$

where $N\alpha = -k \log a$ (this constant has to be proportional to N in order that F should have the additive property); u_0 and α are generally speaking some functions of the volume.

From (34.2) we find (using $E = F - T\,dF/dT$) that the energy of a solid is

$$E = Nu_0 + 3nNkT. \tag{34.3}$$

In other words the equipartition law holds here also: to each variable corresponds an energy $\frac{1}{2}kT$ (not counting the constant Nu_0).

We deduce the specific heat (see 15.6) to be

$$C = Nc = 3Nk, \tag{34.4}$$

where c is the specific heat per molecule. Strictly speaking this specific heat is c_v. However, we shall show below that for a solid the difference between c_v and c_p is not appreciable, so that we are justified in writing the specific heat as simply c. We see that the specific heat is independent of temperature, and also that for all solid bodies containing equal numbers of atoms (e.g. for gram-atomic weights of different elements) the specific heat is the same, independently of the particular nature of the solid (Dulong and Petit's law). Actually this law is applicable for the greater part only to pure elements (and only to some of these) at high temperatures. At low temperatures and for all complicated solids, the law is obeyed very badly.

Substituting (34.4) in (34.2) we obtain

$$F = Nu_0 - NcT\log T + N\alpha T. \tag{34.5}$$

The entropy of a solid body is

$$S = -\partial F/\partial T = Nc\log T + N\beta, \tag{34.6}$$

where $\beta = -\alpha + c$.

We shall now examine in greater detail the quantity α which enters into the expression for F. We have to return to the initial formula (34.1), and substituting the expression for the energy we find

$$F = -kT\log\Big[e^{-Nu_0/kT}\int e^{-f_{\text{II}}(p,q)/kT}\,d\tau_1...d\tau_{nN}\Big].$$

We shall now determine not only the temperature dependence, but also the significance of the temperature independent quantities in this equation.

Choosing as coordinates q_i, the normal coordinates Q_i (and denoting the corresponding momenta by P_i), we can bring the energy, i.e. the function $f_{\text{II}}(p,q)$ into the form

$$\tfrac{1}{2}\sum_i [P_i^2 + \omega_i^2 Q_i^2],$$

where ω_i is the corresponding vibrational frequency. The summation is taken over all the normal modes of vibration of the atoms in the solid, the number of these being, as we have seen, $3nN-6$, or neglecting the 6, $3nN$.

Thus the integral becomes the product of $3Nn$ integrals of the form

$$\iint e^{-(P_i^2+\omega_i^2 Q_i^2)/2kT}\,dP_i\,dQ_i.$$

The integration can be taken between the limits $-\infty$ to $+\infty$ as was explained in § 33, and each of these integrals is then $2\pi kT/\omega_i$.

We obtain in this way

$$F = -kT\log\Big[e^{-Nu_0/kT}(2\pi kT)^{3nN}/\prod_i \omega_i\Big]$$

$$= Nu_0 - 3nNkT\log T - 3nNkT\log 2\pi k + kT\sum_i \log\omega_i.$$

Let $\bar{\omega}$ denote the geometric mean frequency of vibration, defined as the quantity whose logarithm is the mean value of the logarithms of all the frequencies of vibration, i.e.

$$\log\bar{\omega} = \frac{\sum_i \log\omega_i}{3nN}$$

(since the total number of modes of vibration is $3nN$). Introducing this into the above expression for F, and substituting from (34.4), we find

$$F = Nu_0 - NcT\log T + NcT\log(\bar{\omega}/2\pi k). \tag{34.7}$$

$\bar{\omega}$ is, generally speaking, like u_0, some function of volume ($\bar{\omega} = \bar{\omega}(V)$).

From (34.7) we can find the Gibbs free energy G for a solid. Remembering that the temperature T of a solid is relatively low, as was pointed out at the beginning of this section, the second and third terms of (34.7) can be regarded as small corrections to the first term, and using (17.17), we find

$$G = G_0(p) - NcT\log T + NcT\log\{\bar{\omega}(p)/2\pi k\}. \tag{34.8}$$

The volume of the body is thus

$$V = \frac{\partial G}{\partial p} = V_0(p) + \frac{NcT}{\bar{\omega}}\frac{d\bar{\omega}}{dp}, \tag{34.9}$$

where $V_0(p)$ denotes the temperature-independent term $\partial G_0/\partial p$. The second term represents the dependence of the volume on temperature. The temperature-independent coefficient of T, i.e. the quantity $(Nc/\bar{\omega})d\bar{\omega}/dp$, is the coefficient of thermal expansion of the body. It is always positive since the mean frequency $\bar{\omega}$ increases with pressure (when the pressure is increased the atoms in the solid approach each other, the amplitude of their vibration therefore becomes smaller for a given value of the energy, or, in other words, the frequency increases). Thus *solid bodies expand with increase of temperature.*

We can now determine the difference $c_p - c_v$ for a solid; from the

result of Ex. 12, § 18, using the expression (34.9) for the volume, we find

$$c_p - c_v = -\frac{T}{N}\frac{(\partial V/\partial T)_p^2}{(\partial V/\partial p)_T} = -TNc^2\left(\frac{1}{\bar{\omega}}\frac{d\bar{\omega}}{dp}\right)^2 \Big/ \left(\frac{dV_0}{dp}\right). \tag{34.10}$$

This difference, being proportional to T, is in general small compared with c.

EXAMPLE

Find the maximum amount of work, which can be obtained from two identical solid bodies (temperatures T_1 and T_2) by bringing them to a suitable common temperature.

SOLUTION. The solution is quite analogous to that of Ex. 14, § 33. We obtain

$$W_{\max} = Nc\{T_1+T_2-2(T_1T_2)^{\frac{1}{2}}\} = Nc(\sqrt{T_1}-\sqrt{T_2})^2.$$

VI

FLUCTUATIONS AND THERMODYNAMIC INEQUALITIES

35. The thermodynamic inequalities

UP to now (e.g. in § 9) the condition of maximum entropy was written as $dS = 0$. Although this was sufficient for previous purposes, it is not sufficient to determine whether the entropy has a maximum; it is in fact only a condition that the entropy should have an extreme value, i.e. a maximum or minimum, and in order to make it a maximum condition we must take into account the second-order differential.

The entropy is, in general, a function of the energy, the volume, and also of the total momentum of the system, if it moves as a whole. The condition for a maximum of entropy as a function of the total momentum has already been discussed in § 10, where it was shown to be that the temperature should be positive, and so we shall now consider the entropy as a function of only the energy and the volume.

Some necessary conditions for maximum entropy, in particular the vanishing of the first differential of the entropy, have already been investigated in §§ 9, 10, 12, and we obtained as necessary conditions for equilibrium that the temperatures and pressures (and also the velocities) of all parts of the system should be the same. These conditions are, however, not sufficient for equilibrium; but before we investigate the sufficiency conditions we shall introduce another condition, more convenient for the discussion, instead of that of maximum entropy.

Consider the system divided into a number of subsystems in the usual way, then our problem of finding the conditions for equilibrium of the whole system is identical with that of finding the equilibrium conditions for each of the subsystems, since a state of the whole system is determined by the states of its subsystems. As regards each part (subsystem), the remainder of the whole system may be considered as the medium in which this part is situated. We shall show that in equilibrium the quantity $E - T_0 S + p_0 V$ must be a minimum, where E, S, V are the energy, entropy, and volume of the subsystem considered, and T_0, p_0 the temperature and pressure of the medium, i.e. of the remainder of the system. T_0 and p_0 are evidently at the same time the temperature and pressure of the subsystem itself in the equilibrium state.

To prove this we first of all calculate the minimum work which has to be done by a source of work, in order that the subsystem should change from one state to another, the subsystem being immersed in a medium of constant temperature and pressure, T_0 and p_0 respectively. The body (i.e. the subsystem), the source of work, and the medium form a closed system, and the source of work is thermally isolated both from the medium and from the body.

The change of energy of the body in a process of change of state is equal to the work and quantity of heat received by it from the medium together with the work dW done by the source of work. The work and quantity of heat received from the medium are $p_0 dV_0$ and $-T_0 dS_0$ respectively (where the suffix zero means that the quantity refers to the medium; when there is no suffix the quantity refers to the body). Since the total volume (of the system: body plus medium) must be constant

$$dV+dV_0 = 0.$$

Hence the energy change of the body is

$$dE = -p_0 dV-T_0 dS_0+dW.$$

The work taken from the source of work will be minimum if the process is reversible, i.e. if the total entropy remains constant, so that $dS+dS_0 = 0$ (the entropy of the source of work is constant, since it is thermally isolated). Substituting dS for $-dS_0$, we obtain the minimum work as

$$dW = dE+p_0 dV-T_0 dS = d(E-T_0 S+p_0 V), \tag{35.1}$$

and, similarly, the maximum work which can be obtained from the body in a change of state is

$$dW_{max} = -d(E-T_0 S+p_0 V). \tag{35.2}$$

For processes in which $T = T_0$, $V =$ const., or $T = T_0$, $p = p_0$, these results are identical with those of § 17. Similarly to the considerations of § 17, we deduce from these results that, in equilibrium, the quantity $E-T_0 S+p_0 V$ must have a minimum value. This means that for any deviation from equilibrium the change of this quantity must be positive, i.e.

$$\Delta E-T_0 \Delta S+p_0 \Delta V > 0. \tag{35.3}$$

In what follows the coefficients of the differences of thermodynamic

functions from their equilibrium values will always refer to equilibrium values (as in 35.3) and so the suffix zero may be omitted.

Expanding ΔE (E being regarded as a function of S and V) we have

$$\Delta E = \frac{\partial E}{\partial S}\Delta S+\frac{\partial E}{\partial V}\Delta V+\frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\Delta S)^2+2\frac{\partial^2 E}{\partial S\partial V}\Delta S\Delta V+\frac{\partial^2 E}{\partial V^2}(\Delta V)^2\right],$$

neglecting terms of higher than second order. With the help of (12.2) it is easy to see that the first-order terms are just $T\Delta S-p\Delta V$ and so (35.3) gives

$$\frac{\partial^2 E}{\partial S^2}(\Delta S)^2+2\frac{\partial^2 E}{\partial S\partial V}\Delta S\Delta V+\frac{\partial^2 E}{\partial V^2}(\Delta V)^2 > 0, \tag{35.4}$$

and in order that (35.4) should hold for arbitrary ΔS and ΔV the following two conditions are necessary:

$$\frac{\partial^2 E}{\partial S^2} > 0, \tag{35.5}$$

$$\frac{\partial^2 E}{\partial S^2}\frac{\partial^2 E}{\partial V^2}-\left(\frac{\partial^2 E}{\partial S\partial V}\right)^2 > 0. \tag{35.6}$$

Now $$\partial^2 E/\partial S^2 = (\partial T/\partial S)_V = T/C_v,$$

so, since T is always positive, (35.5) becomes

$$C_v > 0. \tag{35.7}$$

The left-hand side of (35.6) can be written as a Jacobian, and so

$$\frac{\partial\{(\partial E/\partial S)_V, (\partial E/\partial V)_S\}}{\partial(S,V)} > 0,$$

or $$\frac{\partial(T,p)}{\partial(S,V)} < 0.$$

Changing to the variables T and V we have

$$\frac{\partial(T,p)}{\partial(S,V)} = \frac{\partial(T,p)}{\partial(T,V)}\bigg/\frac{\partial(S,V)}{\partial(T,V)} = \left(\frac{\partial p}{\partial V}\right)_T\bigg/\left(\frac{\partial S}{\partial T}\right)_V = \frac{T}{C_v}\left(\frac{\partial p}{\partial V}\right)_T < 0.$$

Since by (35.7) $C_v > 0$, this is equivalent to

$$(\partial p/\partial V)_T < 0, \tag{35.8}$$

i.e increase of volume at constant temperature must always be accompanied by a decrease of pressure.

The conditions (35.7) and (35.8) are called the thermodynamic inequalities, and states which do not fulfil these conditions cannot exist in nature.

We may notice that (35.8), together with the formula for $C_p - C_v$ in Ex. 11, § 18, means that

$$C_p - C_v > 0, \tag{35.9}$$

and so by (35.7) we have, also,

$$C_p > 0. \tag{35.10}$$

The conditions (35.7), (35.8) deduced for one of the subsystems hold also for the whole closed system, since in equilibrium the pressures of all the subsystems are the same, provided the system is homogeneous. We must emphasize, however, that the homogeneity condition is essential; consider, for instance, a system whose particles are held together by gravitational forces, then this system will evidently not be uniform, the density becoming greater towards the interior. For a system of this kind the heat capacity C_v might be less than zero, i.e. it could increase its temperature, with a diminution of its energy as a whole. This does not contradict our result that the heat capacity is positive for each small part of the system, since the energy of the whole system in these conditions is not equal to the sum of the energies of its parts, on account of the additional interaction energy of gravitation between the parts.

The inequalities deduced above are the conditions for equilibrium; they are not, however, sufficient to determine whether the state is stable; there may in fact exist a state for which an infinitesimal change of state decreases the entropy, so that the system will tend to return to this state, but for which a finite change of state increases the entropy. After a finite change of this kind, the system will not return to the original state, but will tend to go over into a state of larger entropy, corresponding to a maximum entropy larger than that of the original state. Because of this possibility we have to distinguish between *metastable* and *stable* states of statistical equilibrium. The former of these are states of the kind just considered, i.e. after a sufficiently large deviation from a metastable state, the system will not tend to return to this state, but they are of course stable within certain limits. A stable state, on the other hand, is one to which the system always returns, sooner or later, after a deviation from it, and is in fact a state of complete statistical equilibrium, corresponding to a maximum of entropy larger than any other possible maximum.

EXAMPLES

1. Find the minimum work that has to be done on a perfect gas to compress it from pressure p_1 to pressure p_2, at a constant temperature equal to that of the surrounding medium ($T = T_0$).

SOLUTION. By (35.1) the minimum work W is equal to the change of the function $E - T_0 S + p_0 V$, i.e.

$$W = E_2 - E_1 - T_0(S_2 - S_1) + p_0(V_2 - V_1)$$

(the suffixes 1 and 2 referring to the gas before and after the compression). In our case $E_1 = E_2$ (since the temperature is constant). The change of entropy is given by (28.10) as

$$S_2 - S_1 = Nk \log(p_1/p_2)$$

and by (28.5) the change of volume is

$$V_2 - V_1 = NkT_0\left(\frac{1}{p_2} - \frac{1}{p_1}\right),$$

so

$$W = NkT_0\left[\log\frac{p_2}{p_1} + p_0\left(\frac{1}{p_2} - \frac{1}{p_1}\right)\right].$$

2. Find the maximum work which can be obtained with the help of a perfect gas obeying the equipartition law, when it is cooled at constant volume from temperature T to T_0, the temperature of the medium.

SOLUTION. From the general formula (35.2) we find

$$W_{\max} = Nc_v(T - T_0) + Nc_v T_0 \log(T_0/T).$$

3. The same as Ex. 2, for a cooling from temperature T to T_0, the temperature of the medium, while the gas at the same time expands in such a way that its pressure changes from p to that of the medium, p_0 (the gas again obeying the equipartition law).

SOLUTION.

$$W_{\max} = Nc_v(T - T_0) + NkT_0 \log\frac{p}{p_0} + Nc_p T_0 \log\frac{T_0}{T} + Nk\left(\frac{Tp_0}{p} - T_0\right).$$

4. Find the maximum work which can be obtained with the help of a solid body, in cooling it from temperature T to T_0, the temperature of the medium (at constant volume).

SOLUTION. $$W_{\max} = Nc(T - T_0) + NcT_0 \log(T_0/T).$$

36. The critical point

In § 35 it was shown that the conditions (35.5) and (35.6) were necessary for (35.4) to be positive, and from them the conditions (35.7) and (35.8) were deduced for the stability of a state. It may happen, however, that we have an equality instead of an inequality sign in (35.6), i.e.

$$\frac{\partial^2 E}{\partial S^2}\frac{\partial^2 E}{\partial V^2} - \left(\frac{\partial^2 E}{\partial S \partial V}\right)^2 = 0, \tag{36.1}$$

while (35.5) still holds. Thus (35.8) also becomes an equality:

$$(\partial p/\partial V)_T = 0, \tag{36.2}$$

while $C_v > 0$. It is easy to see that this will also imply

$$C_p = \infty \tag{36.3}$$

as well as (36.2). This follows at once from the formula for $C_p - C_v$ deduced in Ex. 11, § 18.

In these circumstances we may have either an equality or an inequality sign in (35.4) according to the particular values of ΔS and ΔV, i.e. the second differential of the energy may be positive or zero, and the question as to whether $E - T_0 S + p_0 V$ has a minimum requires further investigation. Points for which (36.1) or (36.2) applies are known as *critical points*, and we must now discuss what other conditions have to be fulfilled at a critical point.

Before going on to this it should be noticed that the case where (35.5) becomes an equality, i.e.

$$\partial^2 E/\partial S^2 = 0 \tag{36.4}$$

or $C_v = \infty$, is impossible, as it would then be impossible to satisfy (35.6) (we shall see below that it is also impossible to have (36.4) and (36.1) holding simultaneously).

We now return to the investigation of the equilibrium conditions when (36.1) applies. Evidently we must consider the particular case when the left-hand side of (35.4) is zero, i.e. when ΔS and ΔV have values which make

$$\frac{\partial^2 E}{\partial V^2}(\Delta V)^2 + 2\frac{\partial^2 E}{\partial S \partial V}\Delta V \Delta S + \frac{\partial^2 E}{\partial S^2}(\Delta S)^2 = 0. \tag{36.5}$$

Using (36.1) this can be rewritten as

$$\frac{1}{(\partial^2 E/\partial S^2)}\left[\frac{\partial^2 E}{\partial S^2}\Delta S + \frac{\partial^2 E}{\partial V \partial S}\Delta V\right]^2 = \frac{1}{(\partial^2 E/\partial S^2)}\left[\Delta\left(\frac{\partial E}{\partial S}\right)\right]^2 = 0,$$

or, since $(\partial E/\partial S)_V = T$, we have

$$(\Delta T)^2/(\partial^2 E/\partial S^2) = 0.$$

It follows that $\Delta T = 0$, i.e. $T = \text{const.}$, and in this way we see that the particular case when ΔV and ΔS satisfy (36.5) ((36.1) holding as well) is the case of equilibrium at constant temperature (the temperatures of all parts of the system equal).

In the previous section it was shown that the condition for equilibrium is given by (35.3) (for any small part of the system), and at constant temperature this condition becomes

$$\Delta F + p\Delta V > 0. \tag{36.6}$$

Expanding ΔF in powers of ΔV (since $\Delta T = 0$) we have

$$\Delta F = \frac{\partial F}{\partial V}\Delta V + \frac{1}{2!}\frac{\partial^2 F}{\partial V^2}(\Delta V)^2 + \frac{1}{3!}\frac{\partial^3 F}{\partial V^3}(\Delta V)^3 + \frac{1}{4!}\frac{\partial^4 F}{\partial V^4}(\Delta V)^4 + \dots.$$

Now $\partial F/\partial V = -p$, and $\partial^2 F/\partial V^2 = -(\partial p/\partial V)_T$; since we are discussing the equilibrium conditions at the critical point, $(\partial p/\partial V)_T = 0$ by (36.2), and so (36.6) becomes

$$\frac{1}{3!}\frac{\partial^3 F}{\partial V^3}(\Delta V)^3 + \frac{1}{4!}\frac{\partial^4 F}{\partial V^4}(\Delta V)^4 + \dots > 0. \tag{36.7}$$

In order that this should hold for arbitrary ΔV, it is necessary that the coefficient of $(\Delta V)^3$ should be identically zero, and since

$$\partial^3 F/\partial V^3 = -(\partial^2 p/\partial V^2)_T$$

we obtain

$$(\partial^2 p/\partial V^2)_T = 0. \tag{36.8}$$

It is also necessary that the coefficient of $(\Delta V)^4$ should be positive, or since $\partial^4 F/\partial V^4 = -(\partial^3 p/\partial V^3)_T$,

$$(\partial^3 p/\partial V^3)_T < 0. \tag{36.9}$$

Equations (36.8) *and* (36.9) *determine the equilibrium conditions when* (36.2) *holds, i.e. for a critical point.* States which satisfy (36.2) but not (36.8) and (36.9) cannot occur in nature.

The critical point is thus determined by the conditions (36.2), (36.8), and (36.9); of these, the first two are two equations with two unknowns (since only two of V, p, and T are independent) and so they determine single points. In other words, *critical points are isolated*, and it is impossible, for instance, to have a continuous series of critical states.

It follows also that it is not possible to satisfy the conditions (36.1) and (36.3) simultaneously, for the condition (36.1) necessarily involves (36.4) and (36.8); if any new condition has to be satisfied as well, we have three equations with two unknowns, for which no solution can in general exist. Together with what we said earlier about the impossibility of satisfying (36.4) without (36.1), we see now that a state with $C_v = \infty$ is never possible.

37. The Le Chatelier-Braun principle

Consider a system in some medium, and let W be the minimum work necessary to bring the system from the equilibrium state to some other given state, so that W must have a minimum when the

given state is that of equilibrium (see §§ 14, 17, 35). Let y be a thermodynamic quantity of the system, such that the condition of minimum W with respect to this quantity, i.e. $\partial W/\partial y = 0$, means that the system is in statistical equilibrium in itself, but not necessarily in equilibrium with the surrounding medium. Further, let x be another thermodynamic quantity of the system such that if besides $\partial W/\partial y = 0$ we have also $\partial W/\partial x = 0$ the system is also in equilibrium with the medium. Let

$$(\partial W/\partial x)_y = X, \qquad (\partial W/\partial y)_x = Y. \tag{37.1}$$

Thus when the system is in complete statistical equilibrium, the work W must have a minimum value, for which the necessary conditions besides

$$X = 0, \qquad Y = 0 \tag{37.2}$$

are

$$(\partial X/\partial x)_y > 0, \qquad (\partial Y/\partial y)_x > 0, \tag{37.3}$$

$$\frac{\partial X}{\partial x}\frac{\partial Y}{\partial y} - \left(\frac{\partial X}{\partial y}\right)^2 > 0 \tag{37.4}$$

(we have of course $(\partial X/\partial y)_x = (\partial Y/\partial x)_y$).

Suppose now that the equilibrium with the medium is disturbed, i.e. x changes so that the first of the conditions (37.2) is no longer fulfilled. If y was to remain constant for the disturbance, then the second of the conditions (37.2) would also no longer hold, i.e. the internal equilibrium would also be disturbed. But internal equilibrium again establishes itself, i.e. when x is changed, y changes in such a way as to keep the second of the conditions (37.2) satisfied. Before internal equilibrium has had time to be restored, i.e. while y is constant, the rate of change of X is determined by $(\partial X/\partial x)_y$, but once this equilibrium is restored it is determined by $(\partial X/\partial x)_{Y=0}$ (i.e. the differentiation is taken for a constant value, equal to zero, of the function Y).

Comparing these two derivatives we find (using the properties of Jacobians explained in the footnote on p. 11)

$$\left(\frac{\partial X}{\partial x}\right)_{Y=0} = \frac{\partial(X,Y)}{\partial(x,Y)} = \frac{\partial(X,Y)}{\partial(x,y)}\bigg/\frac{\partial(x,Y)}{\partial(x,y)} = \left(\frac{\partial X}{\partial x}\right)_y - \left[\left(\frac{\partial X}{\partial y}\right)_x^2\bigg/\left(\frac{\partial Y}{\partial y}\right)_x\right].$$

In the state of complete equilibrium the denominator of the second term on the right-hand side is positive by (37.3), and so, taking account of (37.4), we see that

$$0 < \left(\frac{\partial X}{\partial x}\right)_{Y=0} < \left(\frac{\partial X}{\partial x}\right)_y. \tag{37.5}$$

These inequalities form the substance of the so-called *Le Chatelier-Braun principle.*

We can consider the variation of the quantity x as a measure of the action of some external cause, and X as a measure of the change of the properties of the system produced under the influence of this cause. From (37.5) we see that when equilibrium is restored inside the system, after the action of the external cause which took it out of equilibrium, the derivative $\partial X/\partial x$ diminishes. Thus we can formulate the Le Chatelier-Braun principle in the following way: *When a system in equilibrium is acted on by some external cause which takes it out of equilibrium, it changes its state in such a way as to weaken the effect of this cause.*

It is important to notice that we have assigned x and X to be respectively the measures of the action and its result; if we had assigned them the other way round, we should have had to formulate the Le Chatelier-Braun principle in the reverse way.

We shall now illustrate this interpretation of (37.5) by some examples, and further illustrations will be found later in the book.

The minimum work which must be done on a system of temperature and pressure T and p, immersed in a medium of temperature and pressure T_0 and p_0, to make it change its state, is by (35.1)

$$dW = dE - T_0 dS + p_0 dV.$$

Substituting (12.3) this becomes

$$dW = (T-T_0)\,dS - (p-p_0)\,dV. \tag{37.6}$$

Suppose now that x is the entropy S of the system and y is any other thermodynamic quantity, then $X = T-T_0$, as can be seen from (37.6). The condition $X = 0$ gives $T = T_0$, i.e. equality of temperature of all parts of the system, and the inequalities (37.5) become

$$0 < (\partial T/\partial S)_{Y=0} < (\partial T/\partial S)_y. \tag{37.7}$$

These inequalities have the following meaning. Suppose that the entropy of the system is increased by communicating a quantity of heat to it, thus disturbing the internal equilibrium of the system. Before there has been time for equilibrium to re-establish itself, the variation of temperature will be determined by $(\partial T/\partial S)_y$. Immediately after the disturbance from equilibrium, however, processes will begin tending to restore equilibrium, and when these are complete the variation of temperature will be determined by $(\partial T/\partial S)_{Y=0}$. Equation (37.7) shows that the restoration of equilibrium takes

place in such a way as to diminish the variation of temperature of the system, caused by the deviation from equilibrium; i.e. it weakens, as it were, the effect of the cause (the heating, in this case) which disturbs the equilibrium.

Suppose next that x is the volume V of the system, and y again any other thermodynamic quantity. Then just as above we have from (37.6) $X = -(p-p_0)$, and in equilibrium $X = 0$, so that $p = p_0$. We then have from (37.5)

$$0 > (\partial p/\partial V)_{Y=0} > (\partial p/\partial V)_y. \tag{37.8}$$

If the system is disturbed from equilibrium by decreasing its volume (at constant temperature), then the pressure of this part increases ($(\partial p/\partial V)$ being always negative (§ 35)). Before equilibrium is re-established, this increase of pressure is determined by $(\partial p/\partial V)_y$, while when equilibrium is restored the increase is determined by $(\partial p/\partial V)_{Y=0}$. Thus (37.8) shows that the absolute value of the rate of increase diminishes, and in this case, again, the restoration of equilibrium weakens the effect of the cause (here the decrease of volume) which disturbs the equilibrium.

In conclusion we may note that if in (37.7) we take y to be the volume of the system, then the condition $Y = 0$ means $p = p_0$, i.e. constant pressure. Since $(\partial T/\partial S)_v = T/C_v$ and $(\partial T/\partial S)_p = T/C_p$, we obtain from (37.7) the already familiar result $C_p > C_v > 0$. Similarly, if in (37.8) we take y as the entropy, then the condition $Y = 0$ means $T = T_0$, i.e. constant temperature, and we obtain from (37.8)

$$0 > (\partial p/\partial V)_T > (\partial p/\partial V)_S, \tag{37.9}$$

i.e. the isothermal compressibility is greater than the adiabatic compressibility.

38. The Gaussian distribution

We have already mentioned several times that for a system with a great number of degrees of freedom, such as a macroscopic body, physical quantities are nearly always equal to their mean values, and only very occasionally undergo more or less appreciable deviations from these mean values. Such deviations do, however, occur, and it is interesting to know what is the probability that some physical quantity x has a deviation $\Delta x = x - \bar{x}$ from its mean value. It will be remembered that the importance and frequency of deviations from the mean value is conveniently described by the fluctuation, defined as $\sqrt{\overline{(\Delta x)^2}}$ (see § 2).

Consider a closed system and let x denote some physical quantity characteristic of the state of the system—it may refer in particular to a part of the system (if it refers to the whole system, it must not, of course, be a quantity which is constant by definition for a closed system, such as the energy, for instance). Our problem is to determine the probability that this quantity has a value x different from the mean value x_0, which it has in the state of equilibrium. Let $d\Gamma$ be the element of the phase space of the closed system corresponding to values of x between x and $x+dx$. We know (§ 6) that the probability that the system is found in this volume element, i.e. the probability that x has a value in the given range dx, is proportional to the volume $d\Gamma$ of this element, i.e.

$$dw \propto d\Gamma.$$

Let us denote by $\Delta\Gamma$ the statistical weight (§ 7) of the macroscopic state, for which the mean value of the quantity concerned has just the value x, whose probability we wish to find. Evidently we may write

$$dw \propto \Delta\Gamma \frac{d\Gamma}{\Delta\Gamma},$$

but by (7.7)

$$\Delta\Gamma = e^{\sigma},$$

where σ is the entropy of the system in the particular macroscopic state, so

$$dw \propto e^{\sigma} \frac{d\Gamma}{\Delta\Gamma}.$$

Since the volume of any region of phase space is proportional in particular to the corresponding range of values of x, we have

$$d\Gamma/\Delta\Gamma = dx/\Delta x,$$

where Δx is the range of values of x corresponding to the region $\Delta\Gamma$, and therefore is of the order of magnitude of the fluctuation of x. Thus

$$dw \propto e^{\sigma}\, dx/\Delta x.$$

Both e^{σ} and $1/\Delta x$ are functions of x, but the dependence of the former on x is much more important than the latter, since it is exponential, and we may therefore consider dw as proportional to e^{σ} alone, regarding $1/\Delta x$ as constant, so that

$$dw(x) \propto e^{\sigma}\, dx. \tag{38.1}$$

Now the entropy σ of a closed system must have a maximum for

the state of statistical equilibrium, i.e. in particular when $x = x_0$. Since σ is a function of x, it follows that

$$(\partial\sigma/\partial x)_{x=x_0} = 0, \qquad (\partial^2\sigma/\partial x^2)_{x=x_0} < 0.$$

Thus if we expand σ in a series of powers of $y = x - x_0$, we obtain

$$\sigma = \sigma(x_0) - \frac{\lambda}{2}y^2 + \ldots,$$

where $-\lambda$ denotes the value of the second derivative at $x = x_0$ (λ is then positive). Since the deviation of x from its mean value (i.e. y), just like that of any other physical quantity, is generally speaking very small, we may neglect all higher order terms in the above expansion, and substituting in (38.1) we obtain

$$dw(x) = Ae^{-\frac{1}{2}\lambda y^2}\,dx$$

(since $e^{\sigma(x_0)}$ is a constant). The coefficient A is determined, as usual, by the normalizing condition:

$$A\int\limits_{-\infty}^{\infty} e^{-\frac{1}{2}\lambda y^2}\,dy = 1.$$

We have written dy instead of dx since y differs from x only by the constant x_0, and the integration has obviously to be extended from $-\infty$ to ∞ since x can deviate from x_0 in either direction. Even if y could not assume all values between $-\infty$ and $+\infty$ the integration could nevertheless be taken between these limits, since the integrand diminishes very rapidly with increase of y, and increasing the range of integration has no appreciable effect. This normalization gives

$$A = (\lambda/2\pi)^{\frac{1}{2}}.$$

Substituting this in $dw(x)$ we find

$$dw(x) = (\lambda/2\pi)^{\frac{1}{2}}e^{-\frac{1}{2}\lambda y^2}\,dx, \tag{38.2}$$

which gives the probability that the quantity x has a value differing from its mean value x_0 by an amount between y and $y+dy$. This type of probability distribution is known as a *Gaussian distribution*, and we may notice that it is characterized by a single parameter λ.

As we should expect, this probability has a maximum at $y = 0$, i.e. $x = x_0$, and diminishes rapidly for increase of y either in the positive or negative direction, this diminution being the more rapid the greater the value of λ. In other words the mean value of x is at the same time the most probable value. It should be noticed,

however, that this is true only so long as it is possible to neglect the higher order terms in the expansion of σ in powers of y.

In order to see the physical meaning of λ in (38.2) we determine the square of the fluctuation of x, i.e. $\overline{y^2}$. By the definition of mean values we find†

$$\overline{y^2} = \left(\frac{\lambda}{2\pi}\right)^{\frac{1}{2}} \int\limits_{-\infty}^{\infty} y^2 e^{-\frac{1}{2}\lambda y^2}\, dy = \frac{1}{\lambda},$$

and so $\lambda = 1/\overline{y^2}$.

Substituting in (38.2) the Gaussian distribution becomes

$$dw(x) = \frac{1}{(2\pi\overline{y^2})^{\frac{1}{2}}} e^{-\frac{1}{2}y^2/\overline{y^2}}\, dx. \tag{38.3}$$

From this we see the justification of our qualitative statement that the smaller the fluctuation of x, the sharper the maximum of the probability at $y = 0$, or to put it another way, the less probable are appreciable deviations of x from its mean value.

If we know the fluctuation of a physical quantity x, it is easy to find the fluctuation of any function $f(x)$ of this quantity. Since the deviation y is generally speaking small, we may write

$$\Delta f(x) = y(df/dx)_{x=x_0};$$

so

$$\overline{(\Delta f)^2} = \overline{y^2}(df/dx)^2_{x=x_0}, \tag{38.4}$$

since $(df/dx)_{x=x_0}$ is a constant and can be taken outside the averaging sign.

39. The Gaussian distribution for several quantities

In the last section we discussed the probability of deviations from its mean value of any one physical quantity, i.e. the fluctuation of this quantity. We shall now determine the probability of simultaneous deviations of a number of quantities (again characteristic of some part, or the whole of a closed system) from their respective mean values.

Just as we derived (38.1), we may express the probability that the quantities $x_1, x_2, \ldots, x_n$ have values in the given ranges $dx_1, dx_2, \ldots, dx_n$, as

$$dw(x_1, x_2, \ldots, x_n) \propto e^{\sigma}\, dx_1\, dx_2 \ldots dx_n, \tag{39.1}$$

where σ is the entropy of the whole system in the macroscopic state, for which the mean values of $x_1, x_2, \ldots, x_n$ are just equal to the values whose probabilities we wish to find.

† See footnote on p. 59.

Bearing in mind some further application of the results of this section, it is more convenient to use instead of (39.1) a different expression, which can easily be obtained from it. First of all we may evidently write instead of (39.1)

$$dw \propto e^{\Delta\sigma}\,dx_1...dx_n, \tag{39.2}$$

where $\Delta\sigma$ is the change of entropy for our particular deviation from the state of equilibrium (since (39.2) differs from (39.1) only by a constant factor). For small fluctuations, i.e. small deviations from equilibrium, (39.2) can be expressed differently. Suppose that the entropy of the whole system in equilibrium as a function of the total energy of the system is represented by the curve of Fig. 4.

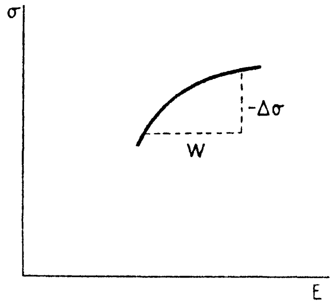


Fig. 4.

If the distance $-\Delta\sigma$ represents the change of entropy in the fluctuation, then evidently the distance W is the minimum work (the work at constant entropy) necessary to take the system out of the state of equilibrium into the given state. On the other hand, $d\sigma/dE = 1/\theta$, where θ is the temperature of the system in equilibrium (we should really write θ_0, but for convenience we leave out the suffix). So from Fig. 4 we see that

$$\Delta\sigma = -W/\theta,$$

and (39.2) becomes

$$dw \propto e^{-W/\theta}\,dx_1...dx_n. \tag{39.3}$$

Just as in § 38, we expand W in powers of

$$y_1 = x_1-x_{10},\quad y_2 = x_2-x_{20},\quad ...,\quad y_n = x_n-x_{n0},$$

where $x_{10}, x_{20},..., x_{n0}$ are the mean values of the quantities $x_1, x_2,..., x_n$. Since in the state of equilibrium W must have a minimum value (equal to zero), the first-order derivatives of W with respect to $x_1, x_2,..., x_n$ are zero at $x_1 = x_{10}, x_2 = x_{20},..., x_n = x_{n0}$, and so, neglecting terms of higher order than quadratic,

$$W/\theta = \sum_{i,k} \tfrac{1}{2}\lambda_{ik}\,y_i\,y_k. \tag{39.4}$$

The quantities λ_{ik} are simply the values of $\dfrac{1}{\theta}\dfrac{\partial^2 W}{\partial x_i\,\partial x_k}$ taken at $x_1 = x_{10}$, etc., and evidently $\lambda_{ik} = \lambda_{ki}$, also since W has a minimum

at $x_1 = x_{10}$, etc., the expression $\lambda_{ik} y_i y_k$ must be essentially positive. Substituting (39.4) in (39.3) we obtain

$$dw = Ae^{-\frac{1}{2}\lambda_{ik} y_i y_k} dx_1 dx_2 ... dx_n.$$

We have omitted the summation sign in the exponent, in accordance with the usual convention, and this should be understood wherever the same index occurs twice, in the rest of this section.

In order to determine the constant A, we must make use of the normalization condition, which, just as in § 38, can be written as

$$A \int_{-\infty}^{\infty} ... \int_{-\infty}^{\infty} e^{-\frac{1}{2}\lambda_{ik} y_i y_k} dy_1 ... dy_n = 1. \tag{39.5}$$

To evaluate this integral we apply that particular linear transformation

$$y_i = \alpha_{ik} y'_k \tag{39.6}$$

which transforms $\lambda_{ik} y_i y_k$ into a sum of squares of y'_m. In order that

$$\lambda_{ik} y_i y_k = y'^2_m,$$

or, as it can be put, $\lambda_{ik} y_i y_k = \delta_{ik} y'_i y'_k$,

(where $\delta_{ik} = 0$ for $i \neq k$ and $= 1$ for $i = k$), the coefficients α_{ik} of the transformation must evidently satisfy

$$\lambda_{ik} \alpha_{il} \alpha_{km} = \delta_{lm},$$

as can be seen by substituting (39.6) in $\lambda_{ik} y_i y_k$. Now it is well known that if we have two determinants $|a_{ik}|$ and $|b_{ik}|$, then the determinant made up of the sums $a_{il} b_{lk}$, i.e. $|a_{il} b_{lk}|$, is equal to the product of the original determinants $|a_{ik}|$ and $|b_{ik}|$, and similarly for any number of determinants. Since the determinant $|\delta_{ik}| = 1$, we deduce from the relation between λ_{ik} and the transformation coefficients that

$$|\lambda_{ik}| \, |\alpha_{ik}|^2 = 1, \tag{39.7}$$

where the two strokes denote a determinant.

Applying this transformation to (39.5) we find

$$A |\alpha_{ik}| \int_{-\infty}^{\infty} ... \int_{-\infty}^{\infty} e^{-\frac{1}{2} y'^2_m} dy'_1 dy'_2 ... dy'_n = 1,$$

since the Jacobian $\quad \dfrac{\partial(y_1, ..., y_n)}{\partial(y'_1, ..., y'_n)} = |\alpha_{ik}|.$

This integral splits up into the product of n integrals, and we obtain

$$A = \frac{1}{|\alpha_{ik}|(2\pi)^{\frac{1}{2}n}}.$$

Making use of (39.7) this becomes

$$A = (2\pi)^{-\frac{1}{2}n}\sqrt{|\lambda_{ik}|}$$

and so the Gaussian distribution for a number of quantities is

$$dw = \frac{\sqrt{|\lambda_{ik}|}}{(2\pi)^{\frac{1}{2}n}} e^{-\frac{1}{2}\lambda_{ik}y_i y_k} dx_1 dx_2 \ldots dx_n \tag{39.8}$$

(we may of course write $dy_1 \ldots dy_n$ instead of $dx_1 \ldots dx_n$). As in the case of one physical quantity, the most probable value of any of the quantities x_i is its mean value x_{i0} (for which $y_i = 0$), which is again because we have confined ourselves to second-order terms in the expansion (39.4).

Since x_{l0} is the mean value of the quantity x_l, we have by the definition of mean values

$$x_{l0} = \sqrt{|\lambda_{ik}|}(2\pi)^{-\frac{1}{2}n} \int \ldots \int x_l e^{-\frac{1}{2}\lambda_{ik}(x_i - x_{i0})(x_k - x_{k0})} dx_1 \ldots dx_n$$

and this can be confirmed by direct integration, if we change the variable from x_l to y_l and integrate from $-\infty$ to ∞. Differentiating this equation with respect to x_{k0}, we find

$$\frac{\sqrt{|\lambda_{ik}|}}{(2\pi)^{\frac{1}{2}n}} \int \ldots \int x_l \lambda_{ki}(x_i - x_{i0}) e^{-\frac{1}{2}\lambda_{ik}(x_i - x_{i0})(x_k - x_{k0})} dx_1 \ldots dx_n = \delta_{lk}.$$

Now the left-hand side is just the mean value of the product $x_l X_k/\theta$, where

$$X_k = \lambda_{ki} y_i \theta = \partial W/\partial y_k = \partial W/\partial x_k. \tag{39.9}$$

Thus

$$\overline{x_i X_k} = \delta_{ik}\theta.$$

Now since $x_i = x_{i0} + y_i$ and $\overline{x_{i0} X_k} = x_{i0}\overline{X_k} = 0$ (by (39.9), since $\bar{y}_i = 0$), this equation is equivalent to

$$\overline{y_i X_k} = \delta_{ik}\theta. \tag{39.10}$$

Substituting (39.9) and changing the suffixes for convenience, we have

$$\lambda_{nl}\overline{y_l y_i} = \delta_{ni}.$$

Multiplying both sides of this equation by λ_{kn}^{-1} (i.e. by the component of the tensor, reciprocal to λ_{kn}) and summing over n, we have

$$\lambda_{kn}^{-1}\lambda_{nl}\overline{y_l y_i} = \lambda_{kn}^{-1}\delta_{ni}.$$

But by the definition of the reciprocal of a tensor

$$\lambda_{kn}^{-1}\lambda_{nl} = \delta_{kl},$$

so

$$\delta_{kl}\overline{y_l y_i} = \lambda_{kn}^{-1}\delta_{ni},$$

and by the definition of δ_{ik}, this reduces to

$$\overline{y_k y_i} = \lambda_{ki}^{-1}. \tag{39.11}$$

Finally, we shall determine also $\overline{X_i X_k}$. By (39.9) and (39.10) we have

$$\overline{X_i X_k} = \lambda_{il} \overline{y_l X_k} \theta = \lambda_{il} \delta_{lk} \theta^2,$$

and so

$$\overline{X_i X_k} = \lambda_{ik} \theta^2. \tag{39.12}$$

If the fluctuations of two of the quantities, say x_1 and x_2, are statistically independent, then as was shown in § 3 the mean value of the product of these fluctuations is zero. Equation (39.11) shows that this occurs if $\lambda_{12}^{-1} = 0$. It can easily be shown that this condition is not only necessary but sufficient, i.e. that if $\lambda_{12}^{-1} = 0$ the fluctuations of the corresponding quantities x_1 and x_2 are independent.

In conclusion we determine the fluctuation of some function $f(x_1,..., x_n)$ of the quantities $x_1,..., x_n$. As in § 36, since the deviations $y_1,..., y_n$ from the mean values are generally small, we may write

$$\Delta f = \frac{\partial f}{\partial x_i} y_i,$$

where by $\partial f/\partial x_i$ we mean the value of the derivative for

$$x_1 = x_{10}, \quad ..., \quad x_n = x_{n0}.$$

Thus

$$\overline{(\Delta f)^2} = \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_k} \overline{y_i y_k}, \tag{39.13}$$

and substituting (39.11)

$$\overline{(\Delta f)^2} = \frac{\partial f}{\partial x_i} \frac{\partial f}{\partial x_k} \lambda_{ik}^{-1}. \tag{39.14}$$

40. Fluctuations of the thermodynamic functions

We shall now determine the fluctuations of the thermodynamic functions of a relatively small part, i.e. a subsystem, of a large closed system. The closed system can be considered as the medium in which the small part is placed, and so we shall speak of the thermodynamic functions sometimes as referring to a system in a medium and sometimes to any small part of a closed system.

Any such subsystem, or a system in a medium, is for nearly all the time in equilibrium with the remainder of the system, or the medium, and its temperature and pressure are thus evidently equal to those of the whole system, or of the medium. We must now find the probability that this subsystem is in some state different from that of equilibrium, for which, consequently, the thermodynamic functions will have values different from those in equilibrium.

In § 39 it was shown that, provided the fluctuation is small, we may express this probability as

$$w \propto e^{-W/\theta}. \tag{40.1}$$

W being the minimum work necessary to take the system out of complete equilibrium into the given state (i.e. to take the given part of the whole system out of equilibrium with the remainder of the system, or with the medium).

In (40.1) we may substitute for W from (35.1), i.e.

$$W = \Delta E - T_0 \Delta S + p_0 \Delta V,$$

where ΔE, ΔS, ΔV are the changes of energy, entropy, and volume of the subsystem, for the deviation from equilibrium, and T_0 and p_0 are the temperature and pressure of the medium, which are evidently also the temperature and pressure of the subsystem itself when in equilibrium with the rest of the closed system, i.e. the medium. Just as in § 35 and § 36 we shall, in what follows, omit the suffix zero in the coefficients of deviations from equilibrium values of thermodynamic functions, and it should be remembered that the values of these coefficients are always equilibrium values. We thus get

$$w \propto e^{-(\Delta E - T\Delta S + p\Delta V)/kT}. \tag{40.2}$$

In this form, this formula applies to any fluctuation of a small part of the system, i.e. both to small and large deviations from the equilibrium state (by large fluctuations we mean such that ΔE, for instance, is comparable with the energy of the given part of the system, but still small, of course, compared with the energy of the whole system). When applied to small fluctuations (such as most often occur) we may expand ΔE in a power series, and, just as in § 35, we obtain

$$\begin{aligned}
\Delta E - T\Delta S + p\Delta V &= \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\Delta S)^2 + 2\frac{\partial^2 E}{\partial S \partial V}\Delta S \Delta V + \frac{\partial^2 E}{\partial V^2}(\Delta V)^2\right] \\
&= \frac{1}{2}\left[\Delta S \Delta \left(\frac{\partial E}{\partial S}\right)_V + \Delta V \Delta \left(\frac{\partial E}{\partial V}\right)_S\right] \\
&= \tfrac{1}{2}(\Delta S \Delta T - \Delta p \Delta V).
\end{aligned}$$

Thus (40.2) becomes

$$w \propto e^{(\Delta p \Delta V - \Delta T \Delta S)/2kT}. \tag{40.3}$$

By means of this general formula we can now find the fluctuations of the various thermodynamic functions. We first of all choose

V and T as independent variables, then (since ΔT, ΔV, etc., are all very small)

$$\Delta S = \left(\frac{\partial S}{\partial T}\right)_V \Delta T + \left(\frac{\partial S}{\partial V}\right)_T \Delta V$$

and

$$\Delta p = \left(\frac{\partial p}{\partial T}\right)_V \Delta T + \left(\frac{\partial p}{\partial V}\right)_T \Delta V.$$

Using the result of Ex. 1, § 18, and (13.4), the first of these relations becomes

$$\Delta S = \frac{C_v}{T}\Delta T + \left(\frac{\partial p}{\partial T}\right)_V \Delta V,$$

and substituting into (40.3) this becomes

$$w \propto \exp\left[-\frac{C_v}{2kT^2}(\Delta T)^2 + \frac{(\partial p/\partial T)_V}{2kT}(\Delta V)^2\right]. \tag{40.4}$$

This expression is the product of two factors, depending respectively on ΔT and ΔV, which means that the probabilities of deviations of temperature and volume from their equilibrium values are independent. In other words, *the fluctuations of temperature and volume are independent.* Thus

$$\overline{\Delta T \Delta V} = 0. \tag{40.5}$$

Comparing each of the factors of (40.4) with the general formula (38.3) for the Gaussian distribution for any physical quantities, we can find the fluctuations both of temperature and volume. Thus

$$\overline{(\Delta T)^2} = kT^2/C_v \tag{40.6}$$

and

$$\overline{(\Delta V)^2} = -kT/(\partial p/\partial V)_T = -kT(\partial V/\partial p)_T. \tag{40.7}$$

We may notice that since $\overline{(\Delta T)^2}$ and $\overline{(\Delta V)^2}$ are essentially positive quantities, the thermodynamic inequalities (35.7) and (35.8) follow at once from (40.6) and (40.7).

Now let us take p and S as independent variables in (40.3), then

$$\Delta V = \left(\frac{\partial V}{\partial p}\right)_S \Delta p + \left(\frac{\partial V}{\partial S}\right)_p \Delta S,$$

$$\Delta T = \left(\frac{\partial T}{\partial S}\right)_p \Delta S + \left(\frac{\partial T}{\partial p}\right)_S \Delta p;$$

but by (15.4)

$$\left(\frac{\partial V}{\partial S}\right)_p = \frac{\partial^2 H}{\partial p \partial S} = \frac{\partial}{\partial p}\left(\frac{\partial H}{\partial S}\right) = \left(\frac{\partial T}{\partial p}\right)_S,$$

and so

$$\Delta V = \left(\frac{\partial V}{\partial p}\right)_S \Delta p + \left(\frac{\partial T}{\partial p}\right)_S \Delta S.$$

Also, by (13.5), we may write

$$\Delta T = \frac{T}{C_p}\Delta S + \left(\frac{\partial T}{\partial p}\right)_S \Delta p.$$

Substituting for ΔV and ΔT in (40.3) we find

$$w \propto \exp\left[\frac{(\partial V/\partial p)_S}{2kT}(\Delta p)^2 - \frac{(\Delta S)^2}{2kC_p}\right]. \tag{40.8}$$

Just like (40.4), this expression is a product of factors depending respectively on Δp and ΔS, and so *the fluctuations of entropy and pressure are independent*, i.e.

$$\overline{\Delta S \Delta p} = 0. \tag{40.9}$$

Comparing (40.8) with (38.3) we obtain the fluctuations of entropy and pressure as

$$\overline{(\Delta S)^2} = kC_p, \tag{40.10}$$

$$\overline{(\Delta p)^2} = -kT\Big/\left(\frac{\partial V}{\partial p}\right)_S = -kT\left(\frac{\partial p}{\partial V}\right)_S. \tag{40.11}$$

The expression (40.7) gives the fluctuation of volume of a part of the system containing some given number of particles N, say. Dividing both sides by N^2 we find the fluctuation of the volume *per particle* as

$$\overline{\left(\Delta \frac{V}{N}\right)^2} = -\frac{kT}{N^2}\left(\frac{\partial V}{\partial p}\right)_T. \tag{40.12}$$

This fluctuation evidently cannot depend on whether we are considering the fluctuation with V constant or with N constant and consequently we can now find the fluctuation of the *number* of particles in a given volume of the system. Since V is constant in this case,

$$\Delta\left(\frac{V}{N}\right) = V\Delta\left(\frac{1}{N}\right),$$

and since ΔN is small, this becomes

$$\Delta\left(\frac{V}{N}\right) = -\frac{V}{N^2}\Delta N;$$

so that, substituting into (40.12), we obtain

$$\overline{(\Delta N)^2} = -\frac{kTN^2}{V^2}\left(\frac{\partial V}{\partial p}\right)_T. \tag{40.13}$$

EXAMPLES

1. Find the fluctuation of energy $\overline{(\Delta E)^2}$ (use V and T as independent variables).

SOLUTION. Expressing ΔE in terms of ΔV and ΔT and using (40.5–7) we find

$$\overline{(\Delta E)^2} = -\{T(\partial p/\partial T)_V - p\}^2 kT(\partial V/\partial p)_T + C_v kT^2.$$

2. Find $\overline{(\Delta H)^2}$ (use p and S as independent variables).

SOLUTION. $$\overline{(\Delta H)^2} = -kTV^2(\partial p/\partial V)_S + kT^2 C_p.$$

3. Find $\overline{\Delta T \Delta p}$ (use V and T as variables).

SOLUTION. Expressing Δp in terms of ΔT and ΔV and multiplying by ΔT we find

$$\overline{\Delta T \Delta p} = \frac{kT^2}{C_v}\left(\frac{\partial p}{\partial T}\right)_V.$$

4. Find $\overline{\Delta V \Delta p}$ (use V and T as variables).

SOLUTION. $$\overline{\Delta V \Delta p} = -kT.$$

5. Find $\overline{\Delta S \Delta V}$ (use V and T as variables).

SOLUTION. $$\overline{\Delta S \Delta V} = -(\partial p/\partial T)_V(\partial V/\partial p)_T kT.$$

6. Find $\overline{\Delta S \Delta T}$ (use V and T as variables).

SOLUTION. $$\overline{\Delta S \Delta T} = kT.$$

7. Find $\overline{(\Delta N)^2}$ for a perfect gas.

SOLUTION. Substituting $V = NkT/p$ in (40.13) we find

$$\overline{(\Delta N)^2} = N.$$

41. Approach to the equilibrium state

Every closed system must sooner or later come into the state of complete statistical equilibrium; let us consider a system which has not yet reached this state. Consider a number of quantities $x_1, x_2, \ldots, x_n$ characteristic of the system as a whole or of its separate parts (in the former case these must, as usual, not be quantities which are constant for a closed system by definition, such as the energy or the volume). The values of these quantities, we shall suppose, completely determine the state of the system, and we shall denote the equilibrium values by $x_{10}, x_{20}, \ldots, x_{n0}$. If the system is not in equilibrium, the quantities will vary with time (i.e. $x_i = x_i(t)$). The speed of variation of x_i for any state is determined by the derivative $\dot{x}_i$, which is a function of the values $x_1, \ldots, x_n$ for this state, i.e.

$$\dot{x}_i = \dot{x}_i(x_1, x_2, \ldots, x_n). \tag{41.1}$$

In the state of equilibrium, we have (see § 39)

$$X_1 = 0, \quad X_2 = 0, \quad \ldots, \quad X_n = 0, \tag{41.2}$$

where, as in § 39, X_i is defined by

$$X_i = \partial W/\partial x_i. \tag{41.3}$$

These conditions must be satisfied for $x_i = x_{i0}$.

Suppose now that the system is in a state close to equilibrium, so that each of the x_i is only slightly different from its equilibrium value x_{i0}, i.e.

$$x_i = x_{i0}+y_i, \tag{41.4}$$

where y_i is a small quantity. If we expand the X_i in powers of the y_i, taking only first-order terms into account, we obtain equations of the form

$$X_i = \alpha_{ik} y_k \tag{41.5}$$

(summation being understood whenever a suffix is repeated). There can be no terms of zero order, since in equilibrium (i.e. for $y_i = 0$) all the X_i must vanish. The coefficients α_{ik} are evidently the derivatives of X_i taken at $x_i = x_{i0}$, i.e.

$$\alpha_{ik} = \frac{\partial X_i}{\partial x_k}\bigg|_{x_1=x_{10},\ldots,x_{n0}=x_n} = \frac{\partial^2 W}{\partial x_i\,\partial x_k}\bigg|_{x_1=x_{10},\ldots,x_n=x_{n0}}.$$

We see therefore that

$$\alpha_{ik} = \alpha_{ki}. \tag{41.6}$$

In a similar way we may expand each of the $\dot{x}_i$ in powers of the y_k, i.e.

$$\dot{x}_i = \beta_{ik} y_k. \tag{41.7}$$

Here, also, there are no terms of zero order, because the rate of change of each x_i must vanish in equilibrium; the coefficients β_{ik} need not, however, be symmetrical with respect to i and k.

If by means of (41.5) we express the y_i in terms of the X_i and substitute in (41.7), then the $\dot{x}_i$ will be expressed as linear functions of the X_i, i.e.

$$\dot{x}_i = \gamma_{ik} X_k. \tag{41.8}$$

We shall now show that *the coefficients γ_{ik}, which we shall call the kinetic coefficients, are symmetrical with respect to i and k*, i.e.

$$\gamma_{ik} = \gamma_{ki}. \tag{41.9}$$

In order to prove this we shall suppose that the deviation of the system is due to a fluctuation. Consider the value of one of the physical quantities, x_i say, at some time t, and the value of another one, x_k, at time $t+\tau$, and take the mean value of the product $x_i(t)x_k(t+\tau)$ with respect to t (for a given value of τ). Now in § 8

it was shown that the fluctuation is symmetrical with respect to future and past, so it is quite immaterial whether in the averaging we take the value of x_k at time τ after or before the moment at which the value of x_i was taken. In other words

$$\overline{x_i(t)x_k(t+\tau)} = \overline{x_i(t+\tau)x_k(t)}. \tag{41.10}$$

Differentiating with respect to τ and putting $\tau = 0$ we obtain

$$\overline{x_i \dot{x}_k} = \overline{\dot{x}_i x_k}. \tag{41.11}$$

We shall now substitute the expression (41.8) for $\dot{x}_i$ into (41.11); since we are here concerned with fluctuations, we cannot of course regard $\dot{x}_i$ as having a definite value for given y_k, but equation (41.8) still remains true if $\dot{x}_i$ there denotes the *average* value of $\dot{x}_i$ for given y_k. It should be noticed also that this average value is defined in terms of the mean rate of change of x_i with *increasing* time, i.e.

$$\bar{\dot{x}}_i = \lim\{[\overline{x_i}(t+\tau)-x_i(t)]/\tau\} \quad (\tau > 0);$$

the derivative defined for $\tau < 0$ has the opposite sign, because of the symmetry of the fluctuation with respect to future and past.

We thus find

$$\overline{x_i \gamma_{kl} X_l} = \overline{\gamma_{il} X_l x_k};$$

but by (39.10)

$$\overline{x_i X_l} = \delta_{il}\theta,$$

and therefore

$$\gamma_{kl}\delta_{il} = \gamma_{ki} = \gamma_{il}\delta_{lk} = \gamma_{ik},$$

which proves (41.9).

From (41.9) and (41.8) it follows that the quantities $\dot{x}_i$ can be expressed in the form

$$\dot{x}_i = -\partial f/\partial X_i, \tag{41.12}$$

where

$$f = -\tfrac{1}{2}\gamma_{ik} X_i X_k. \tag{41.13}$$

Thus the time derivative of the work W can be expressed as

$$\dot{W} = \frac{\partial W}{\partial x_i}\dot{x}_i = X_i \dot{x}_i = -X_i \frac{\partial f}{\partial X_i}.$$

Since f is a quadratic function of the X_i by (41.13), we may apply Euler's theorem and obtain

$$\dot{W} = -2f. \tag{41.14}$$

Quite analogously to the proof of (41.9) it can be shown that if we express the time derivatives of X_i as linear functions of the y_i, i.e.

$$\dot{X}_i = \zeta_{ik} y_k, \tag{41.15}$$

then the coefficients ζ_{ik} are symmetrical, i.e.

$$\zeta_{ik} = \zeta_{ki}. \tag{41.16}$$

We have

$$dW = \frac{\partial W}{\partial x_k} dx_k = X_k dy_k = \alpha_{ki} y_i dy_k = y_i d(\alpha_{ki} y_k)$$
$$= y_i d(\alpha_{ik} y_k) = y_i dX_i$$

(using (41.5) and remembering the symmetry of α_{ik}). Hence

$$(\partial W/\partial X_i) = y_i. \qquad (41.17)$$

At the same time (41.15) may be expressed as

$$\dot{X}_i = -\partial f/\partial y_i \qquad (41.18)$$

on account of (41.16), where

$$f = -\tfrac{1}{2}\zeta_{ik} y_i y_k, \qquad (41.19)$$

so the time derivative, $\dot{W}$, may also be expressed as

$$\dot{W} = \frac{\partial W}{\partial X_i} \dot{X}_i = y_i \dot{X}_i = -y_i \frac{\partial f}{\partial y_i} = -2f.$$

This result is the same as (41.14) and so both functions f, i.e. both (41.19) and (41.13), must be one and the same function, expressed in terms of different variables. Since W must diminish with time, the quadratic form f is essentially positive.

Equation (41.14) may also be written in the form

$$\dot{E} - T\dot{S} + p\dot{V} = -2f, \qquad (41.20)$$

making use of (35.1) for W. For a closed system $E =$ const. and $V =$ const., so (41.20) becomes

$$\dot{S} = 2f/T.$$

Similarly, at constant temperature and volume we have $\dot{F} = -2f$ and at constant temperature and pressure $\dot{G} = -2f$.

42. The dissipation function

The results of § 41 lead, in particular, to important conclusions about the dependence of the forces acting in a system, on the velocities of its moving parts. If we assume these velocities to be small, the forces can be expanded in powers of these velocities; we denote the coordinates of the moving parts by λ_i and the corresponding forces by Λ_i. In this expansion, i.e.

$$\Lambda_i = \Lambda_i^{(0)} + \zeta_{ik}\dot{\lambda}_k + \ldots,$$

the first term is the force acting for $\dot{\lambda}_k = 0$, i.e. for adiabatic motion, and so by § 11, $\Lambda_i^{(0)} = -(\partial E/\partial \lambda_i)_S$; the second term evidently gives the

supplementary forces arising because the process is not completely adiabatic.

The equations of motion are given by

$$\frac{d}{dt}\frac{\partial K}{\partial \dot{\lambda}} = \Lambda_i = \Lambda_i^{(0)} + \zeta_{ik}\dot{\lambda}_k, \tag{42.1}$$

where K is the kinetic energy of the moving parts of the system. Since the entropy and volume of the system at any particular stage of the motion are independent of the velocities, the kinetic energy is the work W which must be done to take the system reversibly for given λ_i from some standard initial state to the given state, i.e. to give it velocities $\dot{\lambda}_i$ (see § 14). Hence $\partial K/\partial \dot{\lambda}_i = \partial W/\partial \dot{\lambda}_i$, and if we take the velocities $\dot{\lambda}_i$ as the quantities x_i introduced above (or as the y_i, which is equivalent since all the velocities vanish in equilibrium), then the $\partial K/\partial \dot{\lambda}_i$ will correspond to the X_i. The equation (42.1) then becomes analogous to (41.15), with the difference that the former includes a term not containing the $\dot{\lambda}_k$ (the term $\Lambda_i^{(0)}$).

We shall see, however, that this difference is not material, and that $\zeta_{ik} = \zeta_{ki}$ holds here, as well as in (41.16). Thus, consider a fluctuation for which a deviation from equilibrium occurs with the given λ_i, such that the velocities assume the values $\dot{\lambda}_i$. Multiplying both sides of (42.1) by one of the velocities, say $\dot{\lambda}_l$, and averaging over the fluctuation, we have

$$\overline{\dot{\lambda}_l \frac{d}{dt}\frac{\partial K}{\partial \dot{\lambda}_i}} = \overline{\dot{\lambda}_l}\Lambda_i^{(0)} + \overline{\dot{\lambda}_l \zeta_{ki}\dot{\lambda}_i}. \tag{42.2}$$

The mean value $\overline{\dot{\lambda}_l}$ (with respect to the fluctuation) of the velocity vanishes, since the probability of the fluctuation is, as we know,

$$w \propto e^{-W/\theta} = e^{-K/\theta},$$

and since K is quadratic in the $\dot{\lambda}_k$, w is an even function of the velocities, so that the integral of $\dot{\lambda}_l w$ vanishes. From this it follows that the first term on the right-hand side of (42.2) must vanish (remembering that $\Lambda_i^{(0)}$, which is a function only of the coordinates λ_k, is constant, since the fluctuation takes place at given λ_k). The rest of the proof (that $\zeta_{ik} = \zeta_{ki}$) is completely analogous to that of (41.9) or (41.16).

We can therefore write the equations of motion (42.1) in the form

$$\frac{d}{dt}\frac{dK}{\partial \dot{\lambda}_i} = \Lambda_i^{(0)} - \frac{\partial f}{\partial \dot{\lambda}_i}, \tag{42.3}$$

where $$f = -\tfrac{1}{2}\zeta_{ik}\dot{\lambda}_i\dot{\lambda}_k.$$

The function f is known as the *dissipation function*, and equations (42.3) are thus *the equations of macroscopic motion for bodies whose motion is accompanied by irreversible processes, or, in other words, whose motion takes place with friction.* Moreover, from the results of § 41 we see that $2f$ is the rate of doing work against the friction.

VII

THE CHEMICAL POTENTIAL

43. Dependence of the thermodynamic functions on the number of particles

THE thermodynamic functions such as energy, entropy, free energy, etc., introduced in Chapter V, are of course functions of the number of particles, i.e. of the number of molecules of the body to which they refer. It is possible to deduce several general propositions about the form of this dependence, independent of the concrete properties of the body, and connected with the *additive property* of most of the thermodynamic functions.

The additive property of energy and entropy has already been pointed out in § 6 and § 7, and since the temperature and pressure of a system in equilibrium are constant throughout the system, the functions F, G, and H are, by definition, also additive. In other words, the values of these functions for a complex system are equal to the sums of their values for the macroscopic parts of the system. In particular, if we increase the size of some uniform system by any factor, the values of E, F, etc., will be increased by the same factor. Since increase of the size of the system means increase of the number of particles, it follows that for systems made up of identical particles, all these functions must be first degree homogeneous functions of the additive variables. Applying this conclusion to the various thermodynamic functions, we obtain the following results.

The energy E is a function of the entropy S and volume V, as well as of N, the number of particles in the system. Both S and V are themselves additive quantities, and so E, as a function of S, V, and N must have the form

$$E = Nf(S/N, V/N), \tag{43.1}$$

which is the most general form of homogeneous function of first degree of N, S, and V.

The Helmholtz free energy F is a function of N, T, and V, and since the temperature is constant throughout the system, while the volume is additive, we can write

$$F = Nf(V/N, T). \tag{43.2}$$

Similarly, we have for the heat function H, which depends on

N, S, and p (remembering that p, like T, is constant throughout the system),

$$H = Nf(S/N, p). \tag{43.3}$$

And finally for the Gibbs free energy G, which is a function of N, p, T,

$$G = Nf(p, T). \tag{43.4}$$

In all the previous chapters we assumed that the number of particles was a given constant, but we shall now regard it as a parameter which can vary in the same way as the other quantities which describe the system. We must therefore introduce an additional term proportional to dN, in the thermodynamic identity (12.3), changing it to

$$dE = T\,dS - p\,dV + \mu\,dN, \tag{43.5}$$

where

$$\mu = (\partial E/\partial N)_{S,V} \tag{43.6}$$

is known as the *chemical potential* of the system. Similarly, the differentials of F, G, and H now become

$$dF = -S\,dT - p\,dV + \mu\,dN, \tag{43.7}$$

$$dG = -S\,dT + V\,dp + \mu\,dN, \tag{43.8}$$

$$dH = T\,dS + V\,dp + \mu\,dN. \tag{43.9}$$

From (43.7–9) it follows that

$$\mu = (\partial F/\partial N)_{V,T} = (\partial G/\partial N)_{p,T} = (\partial H/\partial N)_{p,S}, \tag{43.10}$$

so that the chemical potential can be obtained by differentiation of any one of the functions E, F, G, or H with respect to the number of particles, the result being of course expressed in the variables appropriate to the particular function which has been chosen.

From (43.10) and (43.4) we have that

$$\mu = \partial G/\partial N = f(p, T)$$

and hence

$$G = N\mu(p, T). \tag{43.11}$$

Thus *the chemical potential of a body made up of identical particles is nothing else than the Gibbs free energy per particle.*

In consequence of this (17.12) can be written in the form

$$d\mu = -s\,dT + v\,dp, \tag{43.12}$$

where s and v are the entropy and volume per particle.

44. Equilibrium of systems in a field

If a system is in an external field, different parts of the system will in general be in different external conditions, and so may have different properties. One of the equilibrium conditions of such a

system will be as before constancy of temperature throughout the system; the density and pressure may now, however, be different in different parts of the system. In order to obtain the second equilibrium condition, consider the transfer of molecules from one particular part of the system to another, the state of the rest of the system remaining unchanged. The total number of particles $N = N_1+N_2$, of the two parts, remains constant; let the total entropy of the two parts be $S = S_1+S_2$, then one of the necessary conditions for S to be a maximum is

$$\left(\frac{\partial S_1}{\partial N_1}\right) dN_1 + \left(\frac{\partial S_2}{\partial N_2}\right) dN_2 = 0,$$

but since $dN_1+dN_2 = 0$, this becomes

$$(\partial S_1/\partial N_1 - \partial S_2/\partial N_2)\, dN_1 = 0,$$

or

$$\partial S_1/\partial N_1 = \partial S_2/\partial N_2.$$

From (43.5) we see that the derivative of entropy with respect to the number of particles is $-\mu/T$, so we obtain

$$\mu_1/T_1 = \mu_2/T_2,$$

and since the temperatures of all parts of a system in equilibrium are equal, $T_1 = T_2$, and

$$\mu_1 = \mu_2.$$

Thus for a non-uniform system in equilibrium we must have besides the condition of constant temperature the condition

$$\mu = \text{const.}, \qquad (44.1)$$

i.e. the chemical potentials of different parts of the system must be equal. The chemical potential of each part is a function of its temperature and pressure and also of the parameters specifying the external conditions. If the external conditions are everywhere the same, the constancy of μ and T throughout the system automatically implies constant pressure in the system.

As was mentioned in § 26 the potential energy u of a molecule in a field very often depends only on its position as a whole in space (and not on the positions of the atoms within the molecule). In this case the physical properties of the body at given temperature and pressure will be independent of its position, and the only effect of the external field will be to change the energy of the body. We may then write

$$\mu = \partial E/\partial N = \partial E_0/\partial N + u = \mu_0(p, T) + u,$$

where μ_0 is the chemical potential in the absence of a field (i.e. for $u = 0$). Thus for a system in an external field we must have by (44.1)

$$\mu_0(p, T)+u = \text{const.} \tag{44.2}$$

This condition can be written in differential form, differentiating with respect to coordinates,

$$d\mu_0(p, T)+du = 0,$$

or since $d\mu_0 = -s\,dT + v\,dp$, by (43.12), and the temperature in this case is constant throughout the system (one of the equilibrium conditions),

$$v\,dp+du = 0. \tag{44.3}$$

For a perfect gas we have by (28.8)

$$\mu_0(p, T) = kT \log p+\chi(T).$$

Substituting this into (44.2) we obtain

$$kT \log p+\chi(T)+u = \text{const.},$$

or since T is constant,

$$p = \text{const.}\, e^{-u/kT},$$

which is just Boltzmann's equation (see (26.2)).

45. Mechanical equilibrium

In the preceding section we found the conditions of statistical equilibrium for a system in an external field. For such a system there may, however, exist states which, although not states of statistical equilibrium, do not involve any macroscopic motion of the parts of the system, and the system is then said to be in *mechanical equilibrium*. We shall now investigate the conditions for this to occur.

Consider some part of the system moving (macroscopically) with velocity v, and suppose further that this motion takes place reversibly and in thermal isolation, or, in other words, that the process is an adiabatic one, the entropy of the given part remaining constant. During its motion the given part of the system goes over from one set of stationary external conditions to another. It was shown in § 16 that for this kind of motion the total heat function (of the given part of the system) remains constant; the total heat function is $H_{\text{tot}} = E_{\text{tot}}+pV$, where E_{tot} is the total energy of the given part, and

includes the potential energy in the external field. Thus instead of (16.3) we may write in this case

$$H+\tfrac{1}{2}Mv^2+U = \text{const.}, \tag{45.1}$$

where U is the potential energy of the given part.

In ordinary mechanics the system is in mechanical equilibrium when its potential energy (i.e. its energy minus its kinetic energy) has a stationary value, and the equilibrium is stable if this is a minimum value. From equation (45.1) we see that in the present case the function $H+U$ plays the part which the potential energy plays in ordinary mechanics, and we conclude that in the state of mechanical equilibrium $H+U$ must have a stationary value, or, in other words, that

$$dH+dU = 0, \tag{45.2}$$

where dH is taken at constant entropy (since the motion has been assumed adiabatic). On account of the relation $dH = T\,dS+V\,dp$, the condition (45.2) can be rewritten as

$$Vdp+dU = 0. \tag{45.3}$$

The differentiation in this equation is, of course, with respect to the coordinates of the given part of the system, i.e. with respect to its various positions in space.

The condition for mechanical equilibrium that (45.3) should hold for every part of the system is identical with the condition (44.3) which was derived as the condition for statistical equilibrium of a system in an external field. For statistical equilibrium it is, however, necessary in addition that the temperature should be constant throughout the whole system, while this is not necessary for mechanical equilibrium.

If there is no external field, i.e. $U = 0$, then (45.3) becomes simply $dp = 0$, i.e. for mechanical equilibrium of a system in no external field the pressure must be constant throughout the system.

The condition (45.2) is not, however, sufficient for the equilibrium to be stable since it means only that $H+U = H'$ may have either a minimum or a maximum. We shall now find the condition for the mechanical equilibrium to be stable, i.e. the sufficient condition for H' to have a minimum value; in this case if the system is disturbed from the equilibrium state, it will tend to return to it.

In order to determine this condition consider any two parts of the given system containing equal numbers of particles; let the

entropies of these parts be S_1 and S_2, the pressures in the regions occupied by the two parts be p_1 and p_2, and the coordinates specifying their positions be x_1 and x_2. The pressure will in general be a function of the coordinates, i.e. there is a definite pressure in each region of the system. If the whole system is in mechanical equilibrium, then $dH' = 0$ in every part of it (by (45.2)), the differentiation being with respect to the coordinates of the given part, at constant entropy. In particular this applies to the two given parts of the system, i.e.

$$dH'\{S_1, p(x), x\}|_{x=x_1} = dH'\{S_2, p(x), x\}|_{x=x_2} = 0.$$

Suppose that the first of these two parts moves adiabatically into the place previously occupied by the second, so that its coordinates become x_2, and its pressure p_2, while its entropy remains S_1. In order that the system should be in stable equilibrium, i.e. that H' should have a minimum for each part of the system, it is necessary that $H'(S_1)$ should increase in such a change of position, and, moreover, that for further displacement in the same direction $H'(S_1)$ should continue to increase. This means that $dH'\{S_1, p(x), x\}|_{x=x_2}$ must be positive, and since $dH'\{S_2, p(x), x\}|_{x=x_2} = 0$, we can state this requirement as

$$dH'\{S_1, p(x), x\}|_{x=x_2} = dH'\{S_1, p(x), x\}|_{x=x_2} - dH'\{S_2, p(x), x\}|_{x=x_2} > 0.$$

If the two parts are chosen so that $S_1 - S_2$ is small, then in this inequality $dH'\{S_1, p(x), x\}|_{x=x_2}$ can be expanded in powers of $(S_1 - S_2)$ and we obtain

$$(S_1 - S_2)\, d\frac{\partial H'}{\partial S} > 0.$$

The difference $S_2 - S_1$ has the same sign as the differential dS at the place specified by x_2, since for further displacement of the given part the entropy would continue to change in the same direction (it should be remembered that the differential of the entropy as of all the other functions is with respect to the coordinates, i.e. dS is the difference of entropy of two infinitely close parts of the system, just as $S_2 - S_1$ is the entropy difference of two arbitrary parts of the system). Moreover, $\partial H'/\partial S = \partial H/\partial S = T$, and so the above inequality is equivalent to

$$-dS(dT)_S > 0. \tag{45.4}$$

The differentiation, as in the preceding work, is with respect to the coordinates of the given part, and $(dT)_S$ means the differential of temperature with respect to coordinates at constant entropy (the

temperature being a function of S, p, and x). This condition must be satisfied by every part of the system in order that the system should be in stable equilibrium.

We may point out that unstable mechanical equilibrium leads to the setting up of a macroscopic motion of the parts of the system, called *convection*. Thus the condition of stability is at the same time the condition for absence of convection in the system.

We shall now express (45.4) in a more convenient form. We have

$$(dT)_S = dT - \left(\frac{\partial T}{\partial S}\right)_p dS.$$

Substituting into (45.4) and dividing by $(dS)^2$ we find

$$[dT-(\partial T/\partial S)_p dS]/dS < 0, \tag{45.5}$$

or

$$dT/dS < (\partial T/\partial S)_p. \tag{45.6}$$

This condition is always satisfied if the temperature is constant throughout the system, i.e. $dT/dS = 0$, for $(\partial T/\partial S)_p = T/C_p$ is always positive (since $C_p > 0$ (see § 35)). Hence *convection is possible only if the temperature is not the same in different parts of the system.*

In cases where the external field is of such a nature that its presence does not change the relations between the various thermodynamic functions, the inequality (45.5) can be expressed in a different form. This is always the case if the potential energy of each particle depends only on the position of its centre of gravity in space, but not on its orientation or its internal state; this applies for instance to the gravitational field. For such a case we can write

$$dT = (\partial T/\partial S)_p dS + (\partial T/\partial p)_S dp,$$

and (45.5) becomes $(\partial T/\partial p)_S(dp/dS) < 0$,

or

$$\frac{dS}{dp}\Big/\left(\frac{\partial T}{\partial p}\right)_S < 0. \tag{45.7}$$

Expressing dS in terms of dT and dp, and multiplying both sides of the inequality by the always positive quantity $(\partial T/\partial S)_p = T/C_p$, we have

$$\left[\frac{dT}{dp} - \left(\frac{\partial T}{\partial p}\right)_S\right]\Big/\left(\frac{\partial T}{\partial p}\right)_S < 0,$$

from which we obtain our final *condition for the absence of convection*:

$$\frac{dT}{dp}\Big/\left(\frac{\partial T}{\partial p}\right)_S < 1. \tag{45.8}$$

This formula gives either an upper or a lower limit for dT/dp accord-

ing to the sign of $(\partial T/\partial p)_S = (T/C_p)(\partial V/\partial T)_p$ (see Ex. 15, § 18), i.e. according as to whether the substance expands or contracts with rise of temperature.

In conclusion we determine the limiting value of dT/dz for which convection can occur in an ideal gas in the earth's field of gravity. First of all we rewrite (45.8) in the form

$$\frac{(dT/dz)}{(dp/dz)} \frac{C_p}{T(\partial V/\partial T)_p} < 1, \tag{45.9}$$

where z is the height above the earth. The potential energy of a mass M of gas is $U = Mgz$, and so (45.3) gives

$$V\,dp + Mg\,dz = 0,$$

or

$$dp/dz = -Mg/V.$$

Also, from Clapeyron's equation we have $(\partial V/\partial T)_p = Nk/p$, so we obtain as the condition that convection should not occur

$$|\partial T/\partial z| < Mg/C_p,$$

or

$$|\partial T/\partial z| < mg/c_p, \tag{45.10}$$

where m is the mass of a molecule.

46. The Gibbs distribution for a system with a variable number of particles

In the Gibbs distribution deduced in § 20, as in all the results of the preceding chapters, the number of particles in the system was assumed constant. These results, however, no longer hold if the number of particles can vary, and we shall now deduce the distribution formula for systems in which the number of particles can assume a variety of values. Just as before, we shall suppose all the particles to be identical.

We make use of equation (20.2) giving the probability that some part of a closed system should be found in the element $d\Gamma$ of its phase space. However, the entropy σ of the remainder of the system must now be considered as a function not only of the energy but also of the number of particles. Thus if we want the probability dw_N for a state of the given part of the system, in which this part contains N particles and is to be found in the element $d\Gamma_N$ of its phase space, the entropy σ' must be considered as a function of the energy $E_0 - E(p,q)$ of the remainder of the system, and also of $N_0 - N$, the number of particles in this remainder (N_0 being the

number of particles in the whole system). Notice that an element of phase space of the given part must now be written with a suffix N, since the phase space is different (i.e. it has a different number of dimensions) for different numbers of particles. We thus obtain the result

$$dw_N \propto e^{\sigma'\{E_0 - E(p,q); N_0 - N\}} d\Gamma_N. \tag{46.1}$$

The most important case to consider is when the given part always has an energy much smaller than the energy E_0 of the whole closed system, and the number of particles it contains is small compared with the total number of particles in the system. In this case σ' can be expanded in powers of $E(p, q)$ and N, and only the first-order terms need be retained. This gives

$$dw_N = A e^{\{\mu N - E(p,q)\}/\theta} d\Gamma_N;$$

Introducing instead of A a new constant defined by $A = e^{\Omega/\theta}$ we obtain the Gibbs distribution for a system with a variable number of particles in the form

$$dw_N = e^{\{\Omega + \mu N - E(p,q)\}/\theta} d\Gamma_N. \tag{46.2}$$

The distribution function or probability density defined by

$$dw_N = \rho_N \, d\Gamma_N$$

is consequently

$$\rho_N = e^{\{\Omega + \mu N - E(p,q)\}/\theta}. \tag{46.3}$$

ρ_N is a function of all the momenta and coordinates and the number of particles of the given subsystem, hence the normalization condition, i.e. the equality to unity of the sum of all the probabilities, has now to be written as

$$\sum_N \int \rho_N \, d\Gamma_N = \sum_N \int e^{\{\Omega + \mu N - E(p,q)\}/\theta} d\Gamma_N = 1, \tag{46.4}$$

where $\sum_N$ implies summation over all possible numbers of particles in the subsystem. Since $e^{\Omega/\theta}$ does not depend on N or on the momenta or coordinates, it can be taken outside the summation sign. The factor $e^{\mu N/\theta}$ does not depend on the momenta and coordinates, but it does depend on the number of particles, and so can be taken only outside the integration sign. Thus we obtain

$$e^{\Omega/\theta} \sum_N e^{\mu N/\theta} \int e^{-E(p,q)/\theta} d\Gamma_N = 1,$$

so that

$$e^{-\Omega/\theta} = \sum_N e^{\mu N/\theta} \int e^{-E(p,q)/\theta} d\Gamma_N. \tag{46.5}$$

The mean value of any quantity $M_N(p, q)$, which is a function of the

momenta and coordinates and also of the number of particles, is given by

$$\overline{M} = e^{\Omega/\theta} \sum_N e^{\mu N/\theta} \int M_N(p,q) e^{-E(p,q)/\theta}\, d\Gamma_N.$$

We shall now determine the physical meaning of Ω. From the general definition of entropy (7.8), and making use of the distribution (46.3) we find,

$$\sigma = \overline{\log 1/\rho_N} = -[\Omega + \mu\overline{N} - \overline{E(p,q)}]/\theta, \tag{46.6}$$

or

$$\Omega + \mu\overline{N} = \overline{E(p,q)} - \theta\sigma$$

($\overline{N}$ is the mean number of particles in the subsystem). At the same time we have, by definition of the Helmholtz free energy,

$$\overline{E(p,q)} - \theta\sigma = E - \theta\sigma = F,$$

and combining this with the previous equation we obtain the Helmholtz free energy F in the form

$$F = \Omega + \mu\overline{N}. \tag{46.7}$$

From this result we see, incidentally, that if we substitute $\overline{N}$ for N in (46.3) it becomes the Gibbs distribution (27.1). From (46.7) and $\overline{N}\mu = G = F + pV$ we obtain

$$\Omega = -pV. \tag{46.8}$$

It should be noticed that in §43 (in particular in the thermodynamic identities) the number of particles N meant the *mean* number of particles in the given macroscopic state, just as the energy E always implies the mean energy. In this section (and also the next one) the mean number of particles is denoted by $\overline{N}$, but subsequently we shall always omit the bar over the N, as we have already done for the mean energy E.

Differentiating (46.7) we find

$$dF = d\Omega + \mu\, d\overline{N} + \overline{N}\, d\mu.$$

Substituting for dF from (43.7) we obtain:

$$d\Omega = -S\, dT - \overline{N}\, d\mu - p\, dV. \tag{46.9}$$

In other words, the quantity Ω has the nature of a thermodynamic potential with respect to T, μ, and V. In particular

$$\overline{N} = -(\partial\Omega/\partial\mu)_{V,T}. \tag{46.10}$$

By considerations similar to those of § 17 it can easily be shown that for reversible processes at constant T, μ, and V, the work dW done on the system is equal to the change $d\Omega$ of the potential Ω. Since

the system tends to go into a state in which it is incapable of doing work, the potential Ω tends to a minimum in processes at constant T, μ, V, and *in equilibrium* Ω *has a minimum* with respect to such processes.

47. The chemical potential in the Boltzmann distribution

We shall now apply (46.2) to the perfect gas. Consider a small region $\Delta\tau$ in the phase space of a single molecule; this region should be sufficiently small for all the points in it to correspond approximately to one and the same energy, but it need not necessarily contain a large number of molecules.

We shall consider the whole gas as a large closed system, and the assembly of molecules in the region $\Delta\tau$ as a part of this system, and shall apply (46.2) to this part. Let the number of molecules in the part be N, then the energy of this subsystem will be $N\epsilon$, since by definition the interaction between molecules may be neglected for an ideal gas.

Consider the probability w_N that there should be N molecules in the subsystem, i.e. that the region $\Delta\tau$ of the phase space of a molecule should be occupied by N molecules. We must substitute $N\epsilon$ for $E(p,q)$ in (46.2) and $(\Delta\tau)^N/N!$ for $d\Gamma_N$, just as we did in § 29; we then obtain

$$w_N = e^{(\Omega+\mu N-\epsilon N)/\theta}(\Delta\tau)^N/N! = e^{\Omega/\theta}(e^{(\mu-\epsilon)/\theta}\Delta\tau)^N/N!,$$

or, if

$$\nu = e^{(\mu-\epsilon)/\theta}\Delta\tau, \tag{47.1}$$

this becomes

$$w_N = A\nu^N/N!,$$

where A denotes the constant $e^{\Omega/\theta}$; this constant is fixed by the normalization condition, i.e. by the condition that the sum of the probabilities of all possible numbers of particles must be unity. Summing over all values of N from 0 to ∞ we find

$$A\sum_0^\infty \nu^N/N! = Ae^\nu = 1$$

so that $A = e^{-\nu}$ and the expression for w_N becomes

$$w_N = e^{-\nu}\nu^N/N!. \tag{47.2}$$

This equation, then, determines the probability that there should be N molecules in the region $\Delta\tau$ of phase space; it is known as *Smoluchowski's formula.* It is important to notice that it holds for small as well as large values of N.

Since $A = e^{\Omega/\theta}$ and also $A = e^{-\nu}$, we have $\Omega = -\nu\theta$,† or by (47.1)

$$\Omega = -\theta e^{(\mu-\epsilon)/\theta}\,\Delta\tau. \tag{47.3}$$

From this it follows immediately, applying (46.10), that

$$\bar{N} = -\partial\Omega/\partial\mu = e^{(\mu-\epsilon)/\theta}\,\Delta\tau = \nu, \tag{47.4}$$

so that the physical meaning of ν turns out to be the mean number of particles in the region $\Delta\tau$. Thus (47.2) can be rewritten as

$$w_N = e^{-\bar{N}}\bar{N}^N/N!. \tag{47.5}$$

Instead of a finite region $\Delta\tau$, let us now take an infinitesimal element $d\tau$ of phase space, and denote by dN the mean number of particles in this element. Then (47.4) gives

$$dN = e^{(\mu-\epsilon)/\theta}\,d\tau, \tag{47.6}$$

which is evidently identical with the Boltzmann distribution (20.10). Thus we see that the constant C in the Boltzmann distribution is connected with the chemical potential of the gas by the relation

$$C = e^{\mu/\theta}.$$

† The potential Ω here refers to the molecules contained in the region $\Delta\tau$ and should not be confused with the potential Ω for the whole gas, which was used in the previous section.

VIII

PHASE EQUILIBRIUM

48. The conditions for equilibrium of phases

THE state of a homogeneous system can be specified by the values of any two of the thermodynamic quantities, for instance the volume V and energy E, but not all values of V and E correspond to physically possible states. Indeed, we have already seen in § 35 that a physically possible state has to satisfy the thermodynamic inequalities (35.7) and (35.8). It is thus possible to choose values of V and E for which these conditions do not hold and which do not correspond to equilibrium states of the homogeneous system.

In such cases the system ceases to be homogeneous, and generally speaking breaks up into two homogeneous parts in contact with each other, but in different states. *Such states of a substance, which can exist simultaneously in equilibrium and in contact with each other, are known as different phases of the substance.*

We shall now determine the condition for equilibrium of two phases with each other. First of all, just as for any two systems in equilibrium *the temperatures T_1 and T_2 of the two phases must be equal*:

$$T_1 = T_2. \tag{48.1}$$

Further, the condition of *equality of pressures in the two phases* must also be satisfied:

$$p_1 = p_2. \tag{48.2}$$

This is because the pressures of the two phases at their surface of contact must be equal so that the forces exerted by the two phases on each other should be equal and opposite.

Finally, the condition deduced in § 43 *of equality of the chemical potentials of the two phases* must also hold:

$$\mu_1 = \mu_2. \tag{48.3}$$

If the chemical potentials are expressed as functions of the pressures and temperatures of the two phases, (48.3) gives the equation

$$\mu_1(p, T) = \mu_2(p, T),$$

so that the pressure and temperature corresponding to phase equilibrium are functions of each other. Thus two phases cannot be in equilibrium for arbitrary values of p and T, and if the value of one

of these is given, the value of the other for equilibrium is completely determined.

If for instance pressure and temperature are plotted against each other, the points which correspond to phase equilibrium will lie on some curve known as the phase equilibrium curve; points lying on either side of this curve will correspond to uniform states of the substance, i.e. in which it is completely in one or other of the phases. For a change of state of the substance in which the point representing the state crosses the phase equilibrium curve, a splitting up into phases takes place as the curve is crossed, and finally the substance goes completely into the other phase. For slow changes of state of the body, it may sometimes remain uniformly in one phase, even when phase separation should have taken place. A state of this kind is, however, metastable, and it is sufficient for instance to bring the body in this state into contact with the other phase for it to split up rapidly into two phases, and finally transform into the other phase. Examples of this are a supercooled vapour or a superheated liquid.

Quite analogously the conditions for equilibrium of three phases of the same substance with each other are

$$p_1 = p_2 = p_3, \quad T_1 = T_2 = T_3, \quad \mu_1 = \mu_2 = \mu_3. \tag{48.4}$$

Denoting the common pressure and temperature of the three phases as before by p and T, the third condition gives two equations $\mu_1(p,T) = \mu_2(p,T) = \mu_3(p,T)$ with two unknowns p and T, which have as solutions definite pairs of values of p and T. In the pressure-temperature diagram the points in which three phases can coexist will therefore be isolated points (the points of intersection of the phase equilibrium curves for any two of the phases), and such points are known as triple points. It is evidently impossible to have more than three phases of one and the same substance simultaneously in contact.

We shall now determine the so-called *latent heat* for a transition from one phase to another, i.e. the heat which is absorbed or given out when the body transforms from one phase to another. This transition takes place at constant temperature and pressure ((48.1) and (48.2)), and we saw in § 15 (equation (15.1)) that in such processes the quantity of heat is equal to the change of the heat function. Thus the latent heat per molecule of the substance is

$$q = h_2 - h_1, \tag{48.5}$$

where h_1 and h_2 are the values of the heat function per molecule of the substance in the two phases. Since μ is the Gibbs free energy per molecule (for bodies made up of identical molecules), we have $\mu = \epsilon - Ts + pv$ (where ϵ, s, v are the energy, entropy, and volume per molecule). Consequently $\mu_1 = \mu_2$ becomes

$$(\epsilon_2 - \epsilon_1) + p(v_2 - v_1) - T(s_2 - s_1) = (h_2 - h_1) - T(s_2 - s_1) = 0,$$

and so
$$q = T(s_2 - s_1). \tag{48.6}$$

The latent heat of transition is thus equal to the entropy difference of the two phases, multiplied by the temperature at which the transition takes place. The heat q is positive if heat is absorbed in the transition from the first to the second phase (or given out in the reverse transition), while q is negative if heat is given out in the same transition. It should be noticed that (48.6) also follows directly from the relation $q = \int T\,ds$, since T is constant (this formula is applicable here since the transition is evidently a reversible process, the two phases being in equilibrium with each other throughout the transition process).

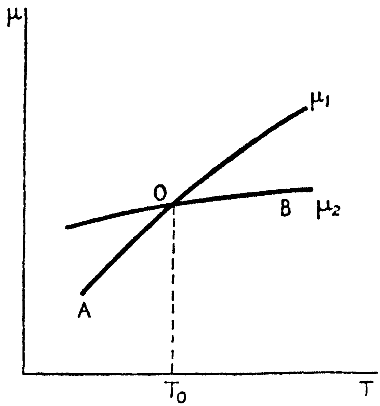


FIG. 5.

Let the two curves in Fig. 5 represent the chemical potential as a function of temperature (at given pressure) for two phases of the same substance. Their point of intersection O defines the temperature T_0 at which the two phases can coexist in equilibrium (for the given pressure). At all other temperatures only one or the other phase can exist. It is easy to see that for temperatures lower than T_0 only the first phase (represented by OA) can exist (i.e. only this phase is stable), while for temperatures higher than T_0 only the second phase (represented by OB) can exist. This follows from the fact that the stable state is the one with the least value of μ (since as we saw in § 17, G tends to a minimum). On the other hand, at the point of intersection O, the derivative $\partial\mu_1/\partial T$ is greater than $\partial\mu_2/\partial T$, i.e. the entropy $s_1 = \partial\mu_1/\partial T$ of the first phase is less than s_2, the entropy of the second, and so the latent heat $q = T(s_2 - s_1)$ is positive. Thus we are led to the conclusion that *if increase of temperature makes the*

substance go from one phase to another, then heat is absorbed in this process. The same result follows also from the Le Chatelier-Braun principle.

EXAMPLES

1. Find the pressure of the saturated vapour over a solid body (the vapour to be considered as a perfect gas, and both gas and solid supposed to obey the equipartition law).

SOLUTION. Substituting the expressions for the chemical potentials of a gas and a solid ((33.6) and (34.5)) into the equilibrium condition $\mu_1 = \mu_2$ (for the solid, G can be replaced by F, since the saturated vapour pressure is so small that pV can be neglected), we find

$$p = \text{const.}\, T^{(c_p - c)/k} e^{(u_{02} - u_{01})/kT}.$$

2. Find the latent heat of transition of a solid into a gas (heat of sublimation). Both gas and solid obey the equipartition law.

SOLUTION. Substituting the expressions (33.9) and (34.3) for the heat functions of a gas and a solid into $q = h_2 - h_1$ (for a solid body F depends very slightly on the volume, and thus the pressure is very small, so that H can be considered as equal to E), we find

$$q = T(c_p - c) + (u_{01} - u_{02}).$$

3. Find the quantity of heat absorbed in the following cyclic process: a body at temperature T is warmed up by dT along the phase equilibrium curve, it then changes into the other phase and is cooled by dT, again along the equilibrium curve. Finally, it changes back into the first phase (thus returning to its initial state).

SOLUTION. The process is evidently reversible, since there is equilibrium throughout. If s_1 and s_2 are the entropies of the two phases, then the quantities of heat absorbed in the successive portions of the cycle will be $T\,ds_1$, $q + dq$, $-T\,ds_2$, $-q$ ($q = T(s_2 - s_1)$ is the latent heat of transition). The total heat absorbed is thus

$$dQ = dq - T(ds_2 - ds_1) = dq - T\,d(q/T) = q\,dT/T.$$

4. Find the entropy of a vapour in equilibrium with a solid (obeying the equipartition law).

SOLUTION. The latent heat of transition from solid to vapour is

$$q = T(s_{\text{vap}} - s_{\text{sol}}).$$

Hence

$$s_{\text{vap}} = q/T + s_{\text{sol}}.$$

The entropy of the solid is $s_{\text{sol}} = c \log T + \beta$ by (34.6); the latent heat has already been calculated in Ex. 2 of this section, and making use of these results, we obtain

$$s_{\text{vap}} = q_0/T + c \log T + \text{const.},$$

where $q_0 = u_{01} - u_{02}$, is the temperature-independent part of the latent heat. At low temperatures the first term is the largest, and approximately

$$s_{\text{vap}} = q_0/T + \text{const.}$$

5. The volume occupied by a solid at temperature T_0 and pressure equal to that of its saturated vapour at T_0 is increased adiabatically until its temperature falls to T. Determine what proportion of it vaporizes (the solid obeys the equipartition law).

SOLUTION. Before cooling, the solid had entropy $S_1(T_0) = Ns_1(T_0)$, where N is the number of particles it contains, and s_1 the entropy per particle. Suppose that $N\nu$ particles vaporize during the expansion, leaving $N(1-\nu)$ in the solid phase. The entropy will now be $N(1-\nu)s_1(T)+N\nu s_2(T)$, where s_2 is the entropy per particle of the vapour. Since the entropy remains constant,

$$Ns_1(T_0) = N(1-\nu)s_1(T)+N\nu s_2(T),$$

or

$$\nu = \frac{s_1(T_0)-s_1(T_1)}{s_2(T)-s_1(T)}.$$

The entropy of the solid is $s_1 = c\log T+\beta$, and the difference s_2-s_1 is q/T, where q is the latent heat at temperature T; so we obtain

$$\nu = \frac{cT}{q}\log\frac{T_0}{T}.$$

6. A vapour at temperature T_0, and having a pressure at which it can exist in equilibrium with a solid of the same temperature, is cooled adiabatically to temperature T. Determine what proportion of it will go into the solid phase

SOLUTION. Quite analogously to the solution of Ex. 5 we find

$$\nu = 1-T/T_0.$$

49. The Clapeyron-Clausius equation

We shall now deduce a number of formulae about the equilibrium of any two phases, making use of the equilibrium condition (48.3) $\mu_1 = \mu_2$; μ_1 and μ_2 are functions of the temperature and pressure (which are equal for both phases), but it should be remembered that these variables are not independent here, since when there is phase equilibrium, the temperature and pressure are related by a function represented by the phase equilibrium curve (§ 48). Thus, differentiating completely with respect to T on both sides of $\mu_1 = \mu_2$, we obtain

$$\frac{\partial\mu_1}{\partial T}+\frac{\partial\mu_1}{\partial p}\frac{dp}{dT} = \frac{\partial\mu_2}{\partial T}+\frac{\partial\mu_2}{\partial p}\frac{dp}{dT}.$$

Applying (43.12) this gives

$$-s_1+v_1\,dp/dT = -s_2+v_2\,dp/dT,$$

or

$$\frac{dp}{dT} = \frac{s_1-s_2}{v_1-v_2}, \tag{49.1}$$

where s_1, v_1 and s_2, v_2 are the entropies and volumes of the two phases per particle.

The difference s_1-s_2 can be conveniently expressed in terms of the

latent heat of transition q. Thus substituting (48.6) into (49.1) we find

$$\frac{dp}{dT} = \frac{q}{(v_2-v_1)T}. \tag{49.2}$$

This result, which is known as the *Clapeyron-Clausius equation*, determines the rate of change of pressure with temperature of two phases in equilibrium, or, in other words, the rate of change of pressure with temperature along the phase equilibrium curve. The same equation (if inverted, i.e. $dT/dp = T(v_2-v_1)/q$) also determines the change of the transition temperature with pressure (for instance, the change of freezing or boiling-point of a liquid with pressure). Since the volume of a gas is always larger than the volume of the same amount of the corresponding liquid, and heat is absorbed in the transition from liquid to gas, we see that the boiling-point temperature is always increased with increase of pressure (dT/dp positive). The freezing-point may, however, be either increased or decreased according as the volume is increased or decreased on melting.

All these consequences of the Clapeyron-Clausius equation are in agreement with the Le Chatelier-Braun principle. Consider for instance a liquid in equilibrium with its saturated vapour, then if the pressure is increased, the boiling-point will be increased according to the Clapeyron-Clausius equation, so that part of the vapour returns to the liquid phase. This in its turn causes a reduction of pressure, i.e. the system as it were opposes the influence taking it out of equilibrium.

Let us consider the special case of (49.2), where one of the phases is a gas which we shall suppose to be perfect. An example of this is any solid or liquid in equilibrium with its vapour (in as far as the vapour can be treated as a perfect gas). Equation (49.2) then determines the variation of the saturated vapour pressure with temperature. The volume of a given mass of the gas is always much greater than the volume of the same mass of the condensed phase (solid or liquid). We may therefore neglect the volume v_1 in comparison with v_2 (the gas being the second phase) and (49.2) becomes

$$dp/dT = q/Tv_2.$$

The volume of the gas can be expressed in terms of its pressure and temperature from Clapeyron's equation, i.e. $v_2 = kT/p$, so we obtain

$$dp/dT = qp/kT^2, \tag{49.3}$$

or

$$d\log p/dT = q/kT^2. \tag{49.4}$$

EXAMPLES

1. Find the specific heat of a vapour along the equilibrium curve of a liquid with its saturated vapour (i.e. the specific heat for a process in which the liquid is always in equilibrium with its saturated vapour). The vapour to be treated as a perfect gas.

SOLUTION. The required specific heat c_s is by the general definition

$$c_s = T\,ds/dT,$$

where ds/dT is the derivative along the equilibrium curve, i.e.

$$c_s = T\frac{ds}{dT} = T\left(\frac{\partial s}{\partial T}\right)_p + T\left(\frac{\partial s}{\partial p}\right)_T\frac{dp}{dT} = c_p - T\left(\frac{\partial v}{\partial T}\right)_p\frac{dp}{dT}.$$

Substituting (49.3) for dp/dT

$$c_s = c_p - q/T.$$

At low temperatures c_s becomes negative, i.e. when heat is removed, the temperature of the vapour has to increase in order that it should remain in equilibrium with the liquid.

2. Find the change of volume of a vapour with temperature for a process in which the vapour is always in equilibrium with the liquid (i.e. along the phase equilibrium curve).

SOLUTION. We require the derivative dv/dT along the equilibrium curve, which is

$$\frac{dv}{dT} = \left(\frac{\partial v}{\partial T}\right)_p + \left(\frac{\partial v}{\partial p}\right)_T\frac{dp}{dT}.$$

Substituting (49.3) and $v = kT/p$ we obtain

$$\frac{dv}{dT} = \frac{1}{p}\left(k - \frac{q}{T}\right).$$

50. The critical point

It was explained in § 48 that the equilibrium of two phases could be described by means of a curve showing the relation between pressure and temperature when the phases coexist in equilibrium. The form of such curves does not, however, usually obey any general laws, and depends on the particular case. In particular these curves may be either closed or open. In the latter case the curve must, generally speaking, finish in some point, as shown for instance in Fig. 6. At temperatures higher than T_c or pressures greater than p_c, different phases can no longer exist, and the substance will remain uniform whatever the value of the othe\ı variable (p or T respectively). Such *an end point of a phase equilibrium curve at which as it were the distinction between phases disappears* is called a *critical point*, and we shall see that it is also a critical point in the sense defined in § 36.

In principle we could also have the case where the phase equilibrium terminated not in the direction of increase of pressure and

temperature (as in Fig. 6) but in the direction of decrease of these variables, i.e. so that no difference of phases could exist *below* a certain temperature and pressure. This kind of critical point has not, however, been found to occur in nature.

Consider the points of a phase equilibrium curve lying near the critical point, i.e. close to the end of the curve, taking V and T as variables. Since at the actual end of the curve the difference between the two phases disappears, the properties of the two phases close to the end must be nearly identical. In particular the volumes of the two phases (for the same number of particles, of course) must be nearly equal, i.e. the difference ΔV between the volumes of these phases must be small. The pressures of the two phases, as we know from § 48, are always equal, so $\Delta p = 0$. Let us expand Δp in powers of ΔV near the critical point, giving

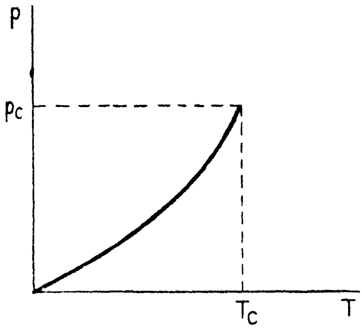


FIG. 6.

$$\Delta p = \left(\frac{\partial p}{\partial V}\right)_T \Delta V + \frac{1}{2}\left(\frac{\partial^2 p}{\partial V^2}\right)_T (\Delta V)^2 + \ldots = 0$$

(the values of the various derivatives referring of course to the critical point). This equation has to have infinitesimally small solutions for V near the critical point, and so it follows that at the critical point we must have

$$(\partial p/\partial V)_T = 0.$$

Thus the end point of the phase equilibrium curve is indeed the critical point as defined in § 36 (36.2), and as was shown in § 36, in order that such a state should be stable, we must have in addition

$$(\partial^2 p/\partial V^2)_T = 0 \quad \text{and} \quad (\partial^3 p/\partial V^3)_T < 0.$$

We shall now examine the properties of bodies in states close to the critical point. If T and V are the temperature and volume of the body, let

$$T - T_c = t, \qquad V - V_c = v, \tag{50.1}$$

where T_c and V_c are the temperature and volume of the body at the

critical point.† Thus we shall consider the properties of the body for small t and v. All the thermodynamic functions can be regarded as functions of t and v, and in particular let us expand $(\partial p/\partial v)_T$ in powers of t and v, retaining only the lowest order terms, i.e.

$$-(\partial p/\partial v)_T = At + Bv^2. \qquad (50.2)$$

There is no term proportional to v, since the coefficient of v is the second derivative of pressure with respect to volume, which is zero at the critical point. As regards the term in tv, this is in any case smaller than the term At, and similarly for the term in t^2. We retain Bv^2, however, since although t and v are both assumed small, nothing is known of their relative magnitudes, so that the term Bv^2 is not necessarily smaller than At. Since at the critical point $\partial^3 p/\partial V^3 < 0$, the coefficient B must be positive:

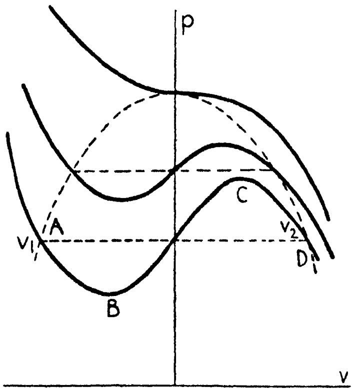


FIG. 7.

$$B > 0. \qquad (50.3)$$

Moreover, at all points in the neighbourhood of the critical point, which represent stable states of the body, we must have, according to § 35,

$$-(\partial p/\partial V)_T > 0.$$

In particular all points with temperature higher than T_c (i.e. $t > 0$) must correspond to stable states (since no division into phases can occur above T_c), so we see that the coefficient A must also be positive:

$$A > 0. \qquad (50.4)$$

From integration of (50.2) we find immediately an expression for the pressure close to the critical point:

$$p = -Atv - \tfrac{1}{3}Bv^3 + \ldots + f(t), \qquad (50.5)$$

where $f(t)$ is a function only of t, which does not interest us at the moment. The pressure as a function of v for given t thus has the appearance shown in Fig. 7, where the upper curve is for temperature T_c (i.e. $t = 0$). At the critical point itself, i.e. at $V = V_c$ ($v = 0$), this curve has a point of inflexion, since we have $(\partial p/\partial v)_t = 0$ and $(\partial^2 p/\partial v^2)_t = 0$, simultaneously.

† In this section, v should not be confused with the volume per particle, which we have used previously.

Consider now points close to the critical point, at which the temperature is less than the critical temperature T_c, i.e. for which t is negative. At some of these points (those which lie on the phase equilibrium curve) both phases may coexist, and then the pressures p_1 and p_2 of the two phases are, as we know, equal. Moreover, the chemical potentials must also be equal to each other ($\mu_1 = \mu_2$), which we can express by

$$\int_1^2 d\mu = 0,$$

where $\int_1^2$ denotes integration along a transition path from a state corresponding to one phase to a state corresponding to the other. If the transition path in the integration is chosen so that T is constant, then this equation is equivalent to

$$\int_1^2 V\,dp = 0. \tag{50.6}$$

We now substitute $V = V_c+v$, and since

$$\int_1^2 V_c\,dp = V_c(p_2-p_1) = 0,$$

we obtain

$$\int_1^2 v\,dp = 0. \tag{50.7}$$

Since we are considering states close to the critical point, we can use the expression (50.5) for p, and it is easy to see that if the integral (50.7) is transformed to the independent variable v (by the substitution $dp = dv(\partial p/\partial v)_t$) the integrand will be an odd function of v.

In order that the integral with respect to v of an odd function of v should be equal to zero, it is sufficient that the volumes (or strictly speaking the differences between the volumes and the critical volume) v_1 and v_2 at the limits of integration, i.e. the volumes (minus V_c) of the two phases in equilibrium with each other, should be equal but of opposite sign, i.e.

$$v_1 = -v_2. \tag{50.8}$$

Since at the same time the pressures of the two phases must be equal, we see that the points representing the states of the two phases in equilibrium (at a given temperature) with each other must be the points A and D in Fig. 7. At the critical temperature these two

points coincide, and become a point of inflexion. The parts of the curve above A and below D correspond to uniform states of the body. For a decrease of pressure (at constant temperature) the point describing the state of the body moves along the upper part of the curve, until at the pressure corresponding to A and D the substance breaks up into two phases. For further reduction of pressure the substance is again uniform, but the point representing its state now moves along the curve below D. At the critical temperature (and higher temperatures) no separation into two phases occurs.

As regards the points on the section BC of the curve in Fig. 7, they do not in general correspond to any stable states of the substance since $(\partial p/\partial v)_T$ is positive along BC. The sections AB and CD correspond to the metastable states discussed in § 48; thus for a slow change of state along the upper part of the curve the body may remain homogeneous in states along AB. These states are, however, metastable, since it is sufficient to bring the body into contact with the other phase for it to break up into two phases. If, for instance, we are dealing with the liquid and gaseous phases, the sections CD and AB correspond to the supercooled vapour and the superheated liquid respectively.

It should be observed that even far away from the critical state a similar state of affairs exists (see the next section). The p, v curve then has a form similar to Fig. 7, but, however, it is not generally speaking symmetrical, as it is when close to the critical point (since (50.5) no longer applies, and in particular (50.8) is then not true).

We have from $p_1 = p_2$ and (50.5), using (50.8),

$$Atv_1 + \tfrac{1}{3}Bv_1^3 = -Atv_1 - \tfrac{1}{3}Bv_1^3,$$

i.e.

$$At + \tfrac{1}{3}Bv_1^2 = 0$$

(and the same of course for v_2). Hence

$$v_1 = -v_2 = -\sqrt{[-3At/B]}. \qquad (50.9)$$

Thus close to the critical point the difference between the volume and critical volume varies as the square root of the difference between the temperature and the critical temperature. This is known as *Mathias's parabolic rule*. If v is plotted against T, then the curve representing the differences from the critical volume of the volumes of the two phases as a function of temperature will be parabolic close to T_c, with a simple maximum at T_c (Fig. 8).

A similar curve will evidently be obtained in the p, v diagram if we connect up the points (such as A, D in Fig. 7) at which phase separation occurs at various temperatures. Farther from the critical point this curve will be no longer parabolic however. All points in Fig. 7 or Fig. 8 lying outside these curves represent states of the body in which it is uniformly in one phase, while the points within these curves represent the region of phase separation. Thus at any point within the curve of Fig. 8 the substance breaks up into two phases, whose states are represented by the points of intersection with the curve, of a line parallel to the axis of abscissae through the point concerned. The quantities of the two phases into which the body splits up will be proportional to the distances along this line between the point and the intersections with the two branches of the curve.

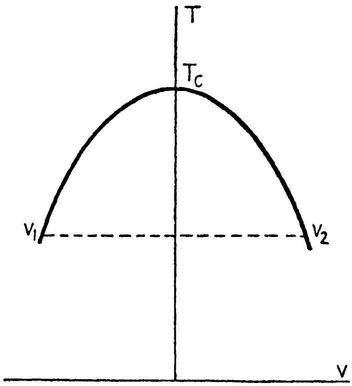


FIG. 8.

We shall next determine the volumes v_1' and v_2' corresponding to the boundaries of the metastable regions (i.e. the points B and C in Fig. 7). Beyond these points $(\partial p/\partial v)_t$ becomes positive, while at the actual points $(\partial p/\partial v)_t = 0$. Using the expression (50.2) we see that v_1' and v_2' are the roots of the equation

$$At + Bv'^2 = 0,$$

so that

$$v_1' = -v_2' = -\sqrt{(-At/B)}. \qquad (50.10)$$

Thus these volumes are $\sqrt{3}$ times smaller than the volumes v_1 and v_2 at which the substance breaks up into two phases (see (50.9)).

In conclusion we determine the variation with temperature of the latent heat close to the critical point. Since the temperatures of the two phases in equilibrium are equal, and the difference of volumes near the critical point is small, we may write

$$Q = T(S_2 - S_1) = T\left(\frac{\partial S}{\partial V}\right)_T (V_2 - V_1) = T\left(\frac{\partial p}{\partial T}\right)_V (V_2 - V_1) \qquad (50.11)$$

(since $(\partial S/\partial V)_T = -\partial^2 F/\partial V \partial T = (\partial p/\partial T)_V$). Close to the critical point we have by (50.9) that $V_2 - V_1$, which is equal to $v_2 - v_1$, is proportional to $\sqrt{(T_c - T)}$, so the latent heat is also proportional to this

root. Further, if we compare (50.11) with the Clapeyron-Clausius equation (49.2), we see that close to the critical point

$$(\partial p/\partial T)_V = dp/dT, \qquad (50.12)$$

where dp/dT is the derivative along the phase equilibrium curve.

In conclusion we shall find how the specific heat C_p varies with temperature close to the critical point for states on the phase equilibrium curve. As we know from § 36, C_p grows infinite at the critical point and in order to find the law of increase we use the formula (Ex. 11, § 18)

$$C_p = C_v - T\left(\frac{\partial p}{\partial T}\right)_V^2 \bigg/ \left(\frac{\partial p}{\partial V}\right)_T.$$

Near the critical point $(\partial p/\partial V)_T = -At - Bv^2$ and v is proportional to $\sqrt{(-t)}$ on the phase equilibrium curve. Consequently C_p grows infinite as $-1/t$, i.e. as $1/(T_c - T)$.

51. Gas and liquid

In this section we shall discuss the equilibrium of a gas with a condensed phase which may be either a liquid or an amorphous solid. Both of these are isotropic, i.e. their properties are identical in all directions (in contrast to crystals). There is no difference in principle between a liquid and an amorphous solid, the latter being distinguished from the former merely by a smaller amplitude of the vibrations of its molecules (as in the definition of solids in § 34). It is only crystalline solids which have other properties that distinguish them fundamentally from liquids, and which we shall discuss in Chapter XI.

Just in the same way, there is no difference in principle between a liquid and a gas, except in the amount of interaction of the molecules, and for this reason a continuous transition between liquid and gas is possible. This means that *the phase equilibrium curve for a liquid and gas* has the form shown in Fig. 6, § 50, i.e. it *has an end point* (*at the critical point*). A continuous transition from liquid to gas (or vice versa) can be achieved if the state is changed along a path avoiding the phase equilibrium curve, i.e. passing above the critical point, but in the course of this process the body will always remain homogeneous. For this reason the conceptions of liquid and gas are only conventional, and it is not always possible to distinguish one from the other, i.e. to say which states are liquid and which gaseous. It is only possible to speak of liquid and gas without ambiguity when they

exist simultaneously in contact with each other, i.e. at points on the phase equilibrium curve, and then the more condensed phase is called the liquid and the less condensed phase the gas.

Qualitatively, this behaviour of liquid and gas is described by van der Waals' equation, obtained in § 32 (equation (32.7)). In order to discuss the properties of this equation we plot the isothermal curves in the p, V diagram which show the relation between p and V at different temperatures (it should be remembered that V is the volume corresponding to some definite number of particles). These isothermals have the form shown in Fig. 9, where curves 1, 2, 3, 4, and 5 refer to progressively increasing temperatures. They have the same general character as the curves of Fig. 7, giving the relation between p and V near the critical point. Thus, for instance, in curve 1 the points A and D correspond to the pressure at which phase separation begins (just as in § 50); the more condensed phase, represented by A, is the liquid, while the less condensed, represented by D, is the gas. The temperature for which curve 1 is the isothermal is the boiling-point temperature for the pressure at A or D (and conversely this pressure is that of the saturated vapour for this temperature). Points on the curve above A are said to correspond to liquid states and below D to gaseous states. The sections AB and CD correspond to the metastable superheated liquid and the supercooled gas respectively, while the section BC does not correspond to any stable state of the substance, since $(\partial p/\partial V)_T$ is positive.

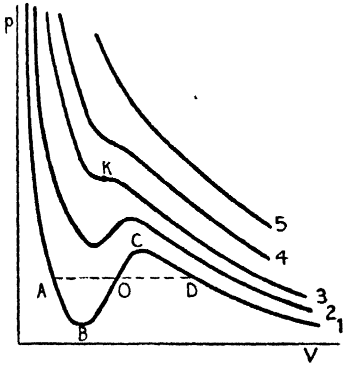


FIG. 9.

As regards the position of the straight line AD, which fixes the gas-liquid transition point, this is determined by the condition of phase equilibrium, which for this purpose is most conveniently expressed in the form given in § 50. Thus (50.6) becomes in the present case

$$\int_{ABOCD} V\,dp = 0. \tag{51.1}$$

This means that the areas ABO and OCD must be equal, which fixes the position of the straight line AD.

At some temperature T_c the p, V curve has a point of inflexion (the point K on curve 3 in Fig. 9), and this must evidently be the critical point. For temperatures above T_c the p, V curves determine V in terms of p as a single-valued function, with $(\partial p/\partial V)_T$ everywhere negative (for instance, curve 4). At such temperatures, consequently, no breaking up into phases is possible, so that the conceptions of liquid and gas lose their meanings.

If all the points (such as A and D) on Fig. 9 which correspond to commencement and conclusion of phase separation are joined together, we obtain the curve shown in Fig. 10. The points on the left and the right of this curve represent liquid and gaseous states respectively, while the shaded area inside corresponds to the separation of the two phases.

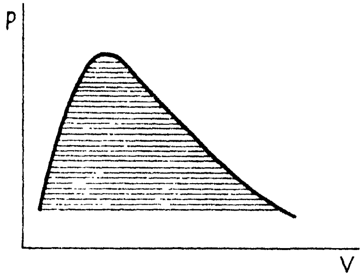


FIG. 10.

The critical temperature T_c, and the corresponding pressure p_c and volume V_c at the critical point, can also be found from van der Waals' equation (32.7). This equation can be written as

$$p = \frac{NkT}{V-Nb} - \frac{N^2a}{V^2}. \tag{51.2}$$

At the critical point we must have $(\partial p/\partial V)_T$ and $(\partial^2 p/\partial V^2)_T$ both zero, so

$$-kT/(V-Nb)^2 + 2Na/V^3 = 0 \tag{51.3}$$

and

$$kT/(V-Nb)^3 - 3Na/V^4 = 0. \tag{51.4}$$

Solving the three equations (51.2–4) for T, V, and p we find

$$T_c = \tfrac{8}{27}a/bk, \quad p_c = \tfrac{1}{27}a/b^2, \quad V_c = 3Nb. \tag{51.5}$$

If now we introduce *reduced* temperatures, pressures, and volumes, defined by

$$\tau = T/T_c, \quad \pi = p/p_c, \quad \nu = V/V_c \tag{51.6}$$

(which are all equal to unity at the critical point), and substitute into van der Waals' equation (making use of (51.5)), the latter assumes the form

$$(\pi + 3/\nu^2)(3\nu - 1) = 8\tau, \tag{51.7}$$

which is the so-called *reduced van der Waals' equation*. This equation contains only τ, π, and ν but no quantities in any way characteristic of the particular substance concerned. Thus (51.7) is the equation of state for all substances to which van der Waals' equation can be

applied. The states of two or more substances, corresponding to the same values of τ, π, and ν, are called *corresponding states* of these substances (the critical states for all bodies are automatically corresponding states). From (51.7) it follows that *if two of the quantities τ, π, ν are the same for different substances, then the third of them must also be the same, i.e. the substances are in corresponding states* (*law of corresponding states*).

If, just as we did for the ordinary van der Waals' equation, we plot π, ν curves, corresponding to equation (51.7), for various values of τ, then these curves must be the same for all substances. Also the straight lines, analogous to *AD* in Fig. 9, and defining the liquid-gas transition point, will evidently be the same for all substances (the position of these lines will now be determined by the condition $\int \nu \, d\pi = 0$, instead of by (51.1)). Hence we conclude that for equal reduced temperatures, all substances have (1) equal reduced saturated vapour pressures, (2) equal reduced volumes of their saturated vapour, and (3) equal reduced volumes in the liquid state in equilibrium with the saturated vapour.

The law of corresponding states can also be applied to the latent heat of vaporization and evidently the 'reduced latent heat' must be a dimensionless quantity, i.e. q/kT_c; we thus obtain

$$q/kT_c = f(T/T_c). \tag{51.8}$$

In conclusion, we should point out that in practice the law of corresponding states applies rather better to actual substances than does van der Waals' equation, since it is not bound up with the detailed form of the equation of state. However, even so, its application is rather limited.

IX
SOLUTIONS

52. Systems with different kinds of particles

UP to now we have limited ourselves to bodies made up of identical particles, and we shall now extend the discussion to systems containing several different kinds of particles. Such systems will include any kind of mixture of several substances, the number of particles of each kind of substance being in general arbitrary. If there is much more of one of the substances than the others, then this mixture is usually called a solution of the other substances (the solutes) in the one that preponderates (the solvent).

As regards chemical compounds, in which the relative numbers of atoms of different species are strictly determined, they are most conveniently treated as systems of identical particles (the molecules). Thus it is usual to describe as the *independent components* (or simply components) of the system only those species of particles whose relative numbers in equilibrium may be arbitrary.

The thermodynamic functions E, F, G, H, etc., for a system with different kinds of particles, are completely determined by the values of two variables such as p and T, together with the numbers of particles of the various independent components.

It is easy to generalize the results of §§ 43, 44, and 46 to include systems of this kind. Firstly, all the thermodynamic functions (such as energy, the free energies, etc.) which are additive must be first-order homogeneous functions of the additive variables, i.e. of the numbers of the various kinds of particles and the volume. Further, in the thermodynamic identities (43.5), (43.7–9) we must now write $\sum_i \mu_i \, dN_i$ instead of the term $\mu \, dN$, where N_i is the number of particles, and μ_i the chemical potential, of the ith species. Correspondingly, the suffix i must be added to the number of particles and the chemical potential in equations (43.6) and (43.10), and in order to find the chemical potential of any one of the substances in the mixed system we must differentiate one of the functions E, F, G, or H with respect to the corresponding number of particles. In particular

$$\mu_i = \partial G / \partial N_i. \tag{52.1}$$

The chemical potential is here expressed as a function of pressure,

temperature, and the concentrations, i.e. of the relative numbers of particles of the various species (these numbers can only enter relatively into μ_i, i.e. as concentrations, because since G is a homogeneous first-order function of the N_i, its derivative with respect to N_i must be a homogeneous zero-order function of the numbers of particles).

From the fact that G is a homogeneous first-order function of the N_i it follows by Euler's theorem that

$$G = \sum_i N_i \partial G/\partial N_i = \sum_i N_i \mu_i, \tag{52.2}$$

which is the generalization of our previous result $G = N\mu$.

The Gibbs distribution (46.3) for systems with different kinds of particles becomes

$$\rho_{N_1,N_2...} = e^{[\Omega + \sum_i \mu_i N_i - E(p,q)]/\theta}, \tag{52.3}$$

and the product $\rho_{N_1,N_2...}\, d\Gamma_{N_1,N_2...}$ is the probability of finding the system in a given element of its phase space, and containing N_1, N_2... particles of the 1st, 2nd... species respectively. Correspondingly, the normalization condition (46.4) now becomes

$$\sum_{N_1} \sum_{N_2} \cdots \int \rho_{N_1,N_2...}\, d\Gamma_{N_1,N_2...} = 1. \tag{52.4}$$

As in § 27, the integration is extended over all physically possible states, and so by $d\Gamma_{N_1,N_2...}$ we mean here the product of the differentials of the coordinates and momenta of all the particles divided by $N_1!\,N_2!\ldots$.

Further, quite analogously to (46.7) we shall now have

$$F = \Omega + \sum_i \mu_i \overline{N_i}, \tag{52.5}$$

so that (46.18) ($\Omega = -pV$) will still be true; this result loses its validity only for bodies in an external field.

The results of § 43 are also easily generalized. Thus the chemical potentials of each species of a system in an external field must be constant throughout the system, i.e.

$$\mu_i = \text{const.} \tag{52.6}$$

Thus if the system contains different kinds of particles, then in equilibrium *the temperature and the n chemical potentials must be constant throughout the system.*

Consider now a system containing a number r of phases in contact with each other, and suppose that the system contains n independent components (each phase will in general contain particles

of all the components). Each phase will then be characterized by the pressure, temperature, and the n chemical potentials (obviously there will be as many chemical potentials as there are independent components).

We already know from § 48 that the condition of phase equilibrium for a system containing only one kind of particle is equality in the phases, of the pressure, temperature, and chemical potential, and evidently in the general case of more than one component this condition becomes the equality of pressure, temperature, and *each* chemical potential. Let the common pressure and temperature of all the phases be p and T; in order to distinguish the chemical potentials of the same species in different phases we shall use an index (with a Roman numeral), while the species of the component will as before be indicated by a suffix (with an Arabic numeral). The condition of phase equilibrium can then be written as

$$\begin{aligned} \mu_1^{\mathrm{I}} &= \mu_1^{\mathrm{II}} = \dots = \mu_1^r, \\ \mu_2^{\mathrm{I}} &= \mu_2^{\mathrm{II}} = \dots = \mu_2^r, \\ &\cdot \quad \cdot \quad \cdot \quad \cdot \\ \mu_n^{\mathrm{I}} &= \mu_n^{\mathrm{II}} = \dots = \mu_n^r. \end{aligned} \tag{52.7}$$

Each of these potentials is a function of $(n+1)$ independent variables, namely p, T and the $(n-1)$ concentrations of the various components in the particular phase (in each phase there are n independent numbers of particles of the different species, and there can be $(n-1)$ independent relations between them).

The conditions (52.7) consist of $n(r-1)$ equations, while there are $2+r(n-1)$ unknowns (p, T and $(n-1)$ concentrations in each phase). In order that these equations should have a solution, it is necessary that the number of equations should not exceed the number of unknowns, i.e.

$$n(r-1) \leqslant 2+r(n-1),$$

hence

$$r \leqslant n+2. \tag{52.8}$$

In other words, *in a system containing n independent components there cannot exist more than* $(n+2)$ *phases simultaneously in equilibrium with each other*. This is the so-called *phase rule* of Gibbs. We have already met with a special case of this rule in § 48, where we saw that in the case of only one independent component there cannot be more than three phases simultaneously in equilibrium with each other.

If r, the number of coexisting phases, is less than $n+2$, then $n+2-r$ of the variables in (52.7) may evidently have arbitrary values. In other words any $n+2-r$ of the variables may be arbitrarily varied without destroying the equilibrium (for such a change the other variables will, of course, vary correspondingly in a completely determined way). The number of variables which can be varied arbitrarily without destroying equilibrium is called the *number of thermodynamic degrees of freedom* of the system. If we denote this number by f, the phase rule can be written in the form

$$f = n+2-r, \tag{52.9}$$

and f can never be negative. If the number of phases has its maximum possible value, $n+2$, then $f = 0$, i.e. all the variables in (52.7) are determined, and none of them can be changed without disturbing equilibrium and making one of the phases disappear.

53. Dilute solutions

We shall now determine the thermodynamic functions for solutions, and shall consider the case of dilute solutions, i.e. such that the number of molecules of the dissolved substances (the solutes) is much less than that of the solvent. We shall limit ourselves at first to the case where only a single substance is dissolved; the results can easily be generalized to the case of more than one dissolved substance.

Let N be the number of molecules of the solvent and n that of the dissolved substance. The ratio $n/N = c$ is called the concentration of the solution, and the above assumption of a dilute solution means $c \ll 1$.

We shall now find an expression for the Gibbs free energy of the solution. Let $G_0(p, T, N)$ be the Gibbs free energy of the pure solvent, i.e. before anything has been dissolved in it, then by (43.11) this can be expressed as $N\mu_0(p, T)$, where μ_0 is the chemical potential of the pure solvent. Suppose now that one molecule of the solute is introduced into the solvent; this will change the Gibbs free energy, but since the change must be very slight, we can assume that the Gibbs free energy becomes

$$G_0+\alpha(p, T, N),$$

where α is some small function. If we introduce a second molecule of the solute, then since the interaction of the two molecules is quite negligibly small, the Gibbs free energy will again be increased by α,

becoming $G_0+2\alpha$. Continuing this process until all the n molecules of the solute have been dissolved, we find that the Gibbs free energy of the solution will be $G_0+n\alpha$ (the interaction of the molecules of the solute can be neglected throughout, because of our assumption that the solution is dilute).

In the expression $G_0+n\alpha$, or $N\mu_0+n\alpha$, obtained in this way we have not, however, made use of the fact that all the n molecules of the solute are identical. On account of their indistinguishability, the state of the system (i.e. of the solution) will not be affected by interchanging the solute molecules with each other. For this reason (just as in § 27) in order to find the statistical weight of a state of the solution, the statistical weight of the state in which the solute molecules are distinguishable must be divided by the number of permutations of the n molecules among themselves, i.e. by $n!$. This will diminish the entropy of the solution by $k\log n!$, while the energy and volume of course remain the same. Now the entropy enters into G in the form $-TS$, so we must add a term $kT\log n!$ to the expression already obtained. Thus

$$G = N\mu_0(p,T)+n\alpha(p,T,N)+kT\log n!.$$

Further, although n is small compared with N, it is nevertheless itself a big number, so Stirling's formula can be applied to the last term (see footnote on p. 69), i.e. the last term can be written as $nkT\log(n/e)$, and

$$G = N\mu_0+n\left(\alpha+kT\log\frac{n}{e}\right) = N\mu_0+nkT\log\left(\frac{n}{e}e^{\alpha/kT}\right). \quad (53.1)$$

We now make use of the fact that G must be a homogeneous first-order function of n and N (see § 52), and for this it is necessary that the function under the log sign in (53.1) should be of zero order in n and N, which means that $e^{\alpha/kT}$ must be of the form $f(p,T)/N$, or

$$G = N\mu_0+nkT\log\left[\frac{n}{eN}f(p,T)\right].$$

Introducing a new function of p and T, defined by

$$\psi(p,T) = kT\log f(p,T),$$

we finally obtain the following expression for the Gibbs free energy of the solution:

$$G = N\mu_0(p,T)+nkT\log[n/eN]+n\psi(p,T). \quad (53.2)$$

The assumption made at the beginning of this argument, about

the addition of a term $n\alpha$ to the Gibbs free energy of the pure solvent, is essentially nothing else than an expansion in powers of n, in which only the first power has been retained. The term of next higher order in n has the form $n^2 f_1(p, T, N)$, and since G must be a homogeneous first-order function of n and N, $f_1(p, T, N)$ must have the form $\beta(p, T)/N$. Thus the general expression for the Gibbs free energy of a solution is

$$G = N\mu_0(p, T) + nkT \log \frac{n}{eN} + n\psi(p, T) + \frac{n^2}{2N}\beta(p, T) + \dots \quad (53.3)$$

For the case of a dilute solution in which a number of different substances are dissolved, the generalization of (53.2) is evidently

$$G = N\mu_0 + \sum_i n_i kT \log \frac{n_i}{eN} + \sum_i n_i \psi_i, \quad (53.4)$$

where n_i is the number of molecules of the ith species of solute. Similarly, the generalization of the higher order approximation (53.3) becomes

$$G = N\mu_0 + \sum_i n_i kT \log \frac{n_i}{eN} + \sum_i n_i \psi_i + \sum_{i,k} \frac{n_i n_k}{2N^2} \beta_{ik}.$$

From equation (53.2) it is easy to find the chemical potential both of the solvent (μ) and of the solute (μ') when they are together in solution. Thus by (52.1), we have for the solvent

$$\mu = \partial G/\partial N = \mu_0 - kTn/N = \mu_0 - kTc, \quad (53.5)$$

while for the solute

$$\mu' = \partial G/\partial n = kT \log(n/N) + \psi = kT \log c + \psi(p, T). \quad (53.6)$$

54. Osmotic pressure

In this and the following sections we shall discuss some of the properties of solutions, on the assumption that the solutions are dilute, so that the formulae of the preceding section can be applied.

Suppose that we have two solutions of the same solute in the same solvent but of different concentrations c_1 and c_2, and that these solutions are separated by a barrier which allows molecules of the solvent to pass, but is impermeable to molecules of the solute (semi-permeable membrane). The pressures exerted on the two sides of the barrier will not be equal (the considerations in § 12 and § 48 about equality of pressure no longer applying on account of the semi-

permeable membrane), and the differences of these pressures is known as the *osmotic pressure.*

The condition for equilibrium between the two solutions will be (in addition to equality of temperature) the equality of the chemical potentials of the solvents on the two sides. The chemical potentials of the solutes need not be equal on the two sides, since on account of the semi-permeable membrane equilibrium can only take place with respect to the solvents.

Denoting the pressures of the two solutions by p_1 and p_2 and applying (53.5), the equilibrium condition can be written as

$$\mu_0(p_1, T)-c_1 kT = \mu_0(p_2, T)-c_2 kT. \tag{54.1}$$

The pressure difference $p_2-p_1 = \Delta p$, i.e. the osmotic pressure, is generally speaking small, so we can expand $\mu_0(p_2, T)$ in powers of Δp and retain only the first two terms:

$$\mu_0(p_2, T) = \mu_0(p_1, T)+\Delta p\, \partial\mu_0/\partial p.$$

Substituting this into (54.1) we find

$$\Delta p\, \partial\mu_0/\partial p = (c_2-c_1)kT,$$

but $\partial\mu_0/\partial p$ is nothing else than the volume v per molecule of the pure solvent, so we have

$$\Delta p = (c_2-c_1)kT/v. \tag{54.2}$$

In particular, if on one side of the barrier we have the pure solvent (i.e. $c_1 = 0$, $c_2 = c$), the osmotic pressure will be

$$\Delta p = ckT/v = nkT/V, \tag{54.3}$$

where n is the number of solute molecules dissolved in a volume V of the solvent (since the solution is dilute, V is also almost exactly equal to the volume of the solution). The result (54.3) is known as *van 't Hoff's equation.* It should be noticed that this equation applies to all weak solutions independently of the nature of either the solvent or the solute. The resemblance to Clapeyron's equation should also be noticed; instead of the gas pressure we have here the osmotic pressure, instead of the volume of the gas, the volume of the solution, and instead of the number of gas molecules, the number of molecules of the dissolved substance.

In conclusion we may remark that the extension of equations (54.2, 3) to the case of several dissolved substances presents no difficulty. Evidently the osmotic pressure in this case will be equal to

the sum of the osmotic pressures for each one of the solutes (i.e. the sum of the pressures if each was dissolved separately).

55. Contact of phases of the solvent

In this section we shall discuss the equilibrium of systems consisting of two contiguous phases of the solvent, each of which contains some amount of the same solute (the solutions are assumed dilute). As we saw in § 52, the equilibrium condition is that besides equality of temperature and pressure, the chemical potentials of the solvent and solute should also be equal in the two phases. Equating the chemical potentials of the solvent (expressed in the form (53.5)) we obtain

$$\mu_0^{\mathrm{I}}(p, T) - c_{\mathrm{I}} kT = \mu_0^{\mathrm{II}}(p, T) - c_{\mathrm{II}} kT, \tag{55.1}$$

where c_{I} and c_{II} are the concentrations of the solute and μ_0^{I} and μ_0^{II} the chemical potentials of the pure solvent in the two phases. It should be noticed that since our system consists of two independent components and two phases, it has two thermodynamic degrees of freedom (see § 52), and so of the four variables p, T, c_{I}, c_{II} only two can be arbitrarily chosen, for instance p or T and one of the concentrations; the other concentration will then be completely determined.

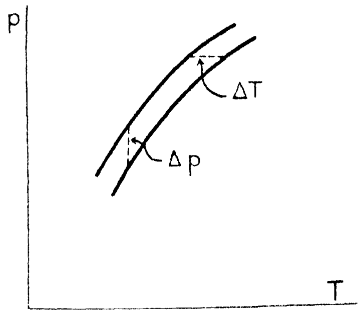


FIG. 11.

If the two phases of the solvent contained no solute molecules, the equilibrium condition would be

$$\mu_0^{\mathrm{I}}(p_0, T_0) = \mu_0^{\mathrm{II}}(p_0, T_0), \tag{55.2}$$

denoting the common pressure and temperature by p_0 and T_0.

Thus if the relation (55.2) between pressure and temperature for phase equilibrium in the pure solvent is represented by one of the curves of Fig. 11, then when some substance has been dissolved in the two phases the relation will change to (55.1) represented by the other curve of Fig. 11, and for dilute solutions these two curves will in general be close to each other.

Let us therefore expand $\mu_0^{\mathrm{I}}(p, T)$ and $\mu_0^{\mathrm{II}}(p, T)$ in (55.1) in powers of $\Delta p = p - p_0$ and $\Delta T = T - T_0$, where p_0 and T_0 are the pressure and temperature at some point of the phase equilibrium curve of the pure solvent, close to a given point (p, T) on the phase equilibrium

curve of the solution. Retaining only first-order powers of Δp and ΔT and using (55.2) we obtain from (55.1)

$$\frac{\partial\mu_0^{\rm I}}{\partial T}\Delta T+\frac{\partial\mu_0^{\rm I}}{\partial p}\Delta p-c_{\rm I}kT = \frac{\partial\mu_0^{\rm II}}{\partial T}\Delta T+\frac{\partial\mu_0^{\rm II}}{\partial p}\Delta p-c_{\rm II}kT.$$

But $-\partial\mu_0^{\rm I}/\partial T$ and $\partial\mu_0^{\rm I}/\partial p$ are just the entropy $s_{\rm I}$ and volume $v_{\rm I}$ per molecule of the first phase of the pure solvent, and similarly $-\partial\mu_0^{\rm II}/\partial T$ and $\partial\mu_0^{\rm II}/\partial p$ are just $s_{\rm II}$ and $v_{\rm II}$ respectively, and on substitution it follows that

$$-(s_{\rm I}-s_{\rm II})\Delta T+(v_{\rm I}-v_{\rm II})\Delta p = (c_{\rm I}-c_{\rm II})kT. \tag{55.3}$$

Now by (48.6) $$(s_{\rm II}-s_{\rm I})T = q,$$

where q is the latent heat of transition per molecule of the pure solvent from the first to the second phase, so (55.3) becomes

$$q\Delta T/T+(v_{\rm I}-v_{\rm II})\Delta p = (c_{\rm I}-c_{\rm II})kT. \tag{55.4}$$

We now consider two special cases of this equation. First of all let us choose the point (p_0, T_0) so that $p_0 = p$, then ΔT will be the distance between the two curves of Fig. 11, parallel to the axis of abscissae, for a given pressure. In other words ΔT will be the change of the temperature of transition between the two phases caused by dissolving the solute, i.e. the difference between the transition temperature T at pressure p when both phases are solutions, and the transition temperature T_0 (at the same pressure p) when both phases are pure. Thus putting $\Delta p = 0$ in (55.4) we obtain

$$\Delta T = kT^2(c_{\rm I}-c_{\rm II})/q. \tag{55.5}$$

In particular, if one of the phases is pure, for instance if $c_{\rm II} = 0$, $c_{\rm I} = c$, then

$$\Delta T = kT^2c/q. \tag{55.6}$$

This formula determines for instance the difference between the freezing-point of a solvent out of solution (when there is no solute in the solid phase) and the freezing-point of the pure solvent, the two phases then being the liquid solution and the solid solvent. Since heat is given out on freezing, q is negative (see § 48), and consequently $\Delta T < 0$. Thus *the freezing-point of a solvent out of solution is lower than that of the pure solvent.*

Similarly, (55.6) determines the change of boiling-point with solution (if the solute does not evaporate), the two phases then being the liquid solution and the vapour of the solvent. ΔT is then the difference of the temperature at which the solvent boils out of solu-

tion and the temperature at which the pure solvent boils, and since heat is absorbed in boiling, $q > 0$ and therefore $\Delta T > 0$. Thus *the boiling-point of a solution is higher than that of the pure solvent.*

Both these consequences of (55.6) are in complete agreement with the Le Chatelier-Braun principle. Thus suppose that the liquid solution is in equilibrium with the solid solvent, then if concentration of the solution is increased, the depression of the freezing-point will bring part of the solid solvent back into the liquid phase, thus reducing the concentration. Consequently, in accordance with the Le Chatelier-Braun principle, the system as it were tends to oppose the influence taking it out of equilibrium. Similarly, if the concentration of the liquid solution in equilibrium with its vapour is increased, the increase of boiling-point brings back some of the vapour into solution and the concentration tends to diminish.

We now consider another special case of (55.4), this time choosing the point (p_0, T_0) so that $T = T_0$; then Δp will be the distance between the two curves parallel to the axis of ordinates, i.e. Δp will be the difference between the equilibrium pressure of the two phases for the solution and for the pure solvent (at the same temperature T). Putting $\Delta T = 0$ in (55.4) we obtain

$$\Delta p = kT(c_{\text{I}}-c_{\text{II}})/(v_{\text{I}}-v_{\text{II}}). \tag{55.7}$$

In particular, this formula may be applied to the equilibrium between liquid and gaseous phases. In this case the volume of one phase (the liquid one) may be neglected in comparison with that of the other, and (55.7) becomes

$$\Delta p = kT(c_{\text{I}}-c_{\text{II}})/v, \tag{55.8}$$

where v is the volume per molecule of the solvent in the gaseous phase (phase I). Substituting $pv = kT$ and $p = p_0+\Delta p$ (where p_0 is the saturated vapour pressure of the pure solvent) (55.8) may be written as

$$\Delta p = p_0(c_{\text{I}}-c_{\text{II}}) \tag{55.9}$$

if we neglect higher order terms in Δp. If the gaseous phase is the vapour of the pure solvent, (55.9) gives

$$\Delta p/p_0 = -c, \tag{55.10}$$

where c is the concentration of the solution. This formula determines the difference of saturated vapour pressure of the solution (p) and the pure solvent (p_0) and is known as *Raoult's rule*: *the relative*

lowering of the saturated vapour pressure is equal to the concentration of the solution.

56. Equilibrium with respect to the solute

The next system which we shall discuss is one consisting of two solutions in contact, which contain concentrations c_1 and c_2 of the same solute but dissolved in *different* solvents (as for instance in two liquids which do not mix).

The equilibrium condition of this system is the equality of the chemical potentials of the solute in the two solutions. Using (52.6) this condition can be expressed as

$$kT\log c_1+\psi_1(p,T) = kT\log c_2+\psi_2(p,T) \tag{56.1}$$

(the functions ψ_1 and ψ_2 are, of course, different for different solvents). Hence

$$c_1/c_2 = e^{(\psi_2-\psi_1)/kT}. \tag{56.2}$$

Thus the solute is distributed between the two solutions in such a way that *the ratio of concentrations* (*at given common temperature and pressure*) *is always the same*, independently of how much solute has been dissolved. The same is evidently true also of the solution of a solute in two contiguous phases of one and the same solvent.

Let us now consider the equilibrium between a gas (which we shall assume perfect) and its solution in some condensed solvent. The equilibrium condition, i.e. equality of the chemical potentials of the pure gas and the gas in solution, is obtained from (53.5) and (28.8), i.e.

$$kT\log c+\psi(p,T) = kT\log p+\chi(T). \tag{56.3}$$

Hence

$$c = pe^{(\chi-\psi)/kT}. \tag{56.4}$$

The function $\psi(p,T)$ characterizes the properties of the liquid (or solid) solution, but at small pressures the properties of a liquid depend very little on pressure, so that the dependence of $\psi(p,T)$ on p is not significant, and we may assume that the factor multiplying p in (56.4) is a (temperature-dependent) constant, independent of pressure, or, at given temperature,

$$c = p\cdot\text{const}. \tag{56.5}$$

Thus *the concentration of a gas in solution is proportional to the pressure of the gas* (only for dilute solutions, of course). This is known as *Henry's law.*

EXAMPLE

Find the variation of concentration with height for a solution in the field of gravity.

SOLUTION. Applying the equilibrium condition (44.2) for a system in an external field to the solute and using (53.6) we find

$$kT\log c+\psi(p, T)+mgz = \text{const.},$$

since the potential energy of a molecule (mass m) of the solute in the field of gravity is mgz at height z. Differentiating with respect to z, and remembering that the temperature is constant (this is one of the equilibrium conditions), we obtain

$$kT\,dc/c + mg\,dz + (\partial\psi/\partial p)\,dp = 0.$$

Since the volume of the solution $\partial G/\partial p = N\partial\mu_0/\partial p+n\partial\psi/\partial p$ (using (53.2) for G), the quantity $\partial\psi/\partial p$ can be called the 'volume' v' occupied by one molecule of the solute, and

$$kT\,dc/c + mg\,dz + v'\,dp = 0.$$

To find the dependence of p on z we may use the equilibrium condition (44.3). For the solvent we have

$$v\,dp + Mg\,dz = 0,$$

where v is the volume per molecule of the solvent, and M the mass of a solvent molecule.

Substituting this into the other equation, we obtain

$$kT\frac{dc}{c}+mg\,dz - Mg\frac{v'}{v}\,dz = 0.$$

If the solution can be assumed incompressible, i.e. v and v' constants, then this gives

$$c = a\exp\Big[-\frac{gz}{kT}\Big(m-\frac{v'M}{v}\Big)\Big],$$

where evidently a denotes the concentration of the solution at the earth's surface (for $z = 0$).

57. Mutual influence of two solutes in solution

Consider a solution of two different solutes in the same solvent, and let their solubilities (i.e. the concentrations of the saturated solutions)† be c'_{01} and c'_{02} when dissolved together and c_{01} and c_{02} when dissolved separately. We shall now find a relation between δc_{01} and δc_{02}, where $c'_{01} = c_{01}+\delta c_{01}$ and $c'_{02} = c_{02}+\delta c_{02}$.

As was shown in § 53, the Gibbs free energy of the solution of the two solutes together is (up to terms of the second order)

$$G = N\mu_0+n_1 kT\log\frac{n_1}{eN}+n_2 kT\log\frac{n_2}{eN}+$$
$$+n_1\psi_1+n_2\psi_2+\frac{n_1^2\beta_{11}}{2N}+\frac{n_2^2\beta_{22}}{2N}+\frac{n_1 n_2\beta_{12}}{N}.$$

† It is assumed, of course, that the saturated solution is still dilute enough for our previous theory to be valid.

Thus the chemical potentials of the two solutes when in solution together are

$$\left.\begin{aligned}\mu_1' = \partial G/\partial n_1 = kT\log c_1+\psi_1+c_1\beta_{11}+c_2\beta_{12},\\ \mu_2' = \partial G/\partial n_2 = kT\log c_2+\psi_2+c_2\beta_{22}+c_1\beta_{12}\end{aligned}\right\} \quad (57.1)$$

(where $c_1 = n_1/N$, $c_2 = n_1/N$). Let μ_{01}' and μ_{02}' be the chemical potentials of the pure solutes; the solubilities c_{01} and c_{02} are determined by the conditions of equilibrium of each of the pure solutes with the corresponding solutes in solution (separately), i.e.

$$\left.\begin{aligned}\mu_{01}' = kT\log c_{01}+\psi_1+c_{01}\beta_{11},\\ \mu_{02}' = kT\log c_{02}+\psi_2+c_{02}\beta_{22}.\end{aligned}\right\} \quad (57.2)$$

Similarly, c_{01}' and c_{02}' are determined by the equilibrium conditions

$$\left.\begin{aligned}\mu_{01}' = kT\log c_{01}'+\psi_1+c_{01}'\beta_{11}+c_{02}'\beta_{12},\\ \mu_{02}' = kT\log c_{02}'+\psi_2+c_{02}'\beta_{22}+c_{01}'\beta_{12}.\end{aligned}\right\} \quad (57.3)$$

Subtracting (57.2) from (57.3), and assuming $\delta c_{01} \ll c_{01}$ and $\delta c_{02} \ll c_{02}$, we have approximately

$$kT\,\delta c_{01}/c_{01} = -c_{02}\beta_{12}, \qquad kT\,\delta c_{02}/c_{02} = -c_{01}\beta_{12}$$

(since $\log c_{01}'-\log c_{01} \simeq \delta c_{01}/c_{01}$ and similarly for δc_{02}), and so we find

$$\delta c_{01} = \delta c_{02}, \quad (57.4)$$

i.e. the changes of solubility of the two solutes are equal.

In a similar way we can determine the changes of saturated vapour pressure of two solutes, when they are dissolved together. Let p_1 and p_2 be the saturated vapour pressures of two solutes of concentrations c_1 and c_2 (when dissolved separately) and $p_1' = p_1+\delta p_1$, $p_2' = p_2+\delta p_2$ be the partial pressures of the same two saturated vapours when dissolved together (with the same concentrations). The chemical potentials of the two vapours are $kT\log p_1+\chi_1(T)$ and $kT\log p_2+\chi_2(T)$, so that p_1 and p_2 are determined by

$$\left.\begin{aligned}kT\log p_1+\chi_1 = kT\log c_1+\psi_1+c_1\beta_{11},\\ kT\log p_2+\chi_2 = kT\log c_2+\psi_2+c_2\beta_{22}.\end{aligned}\right\} \quad (57.5)$$

Similarly, p_1' and p_2' are given by

$$\left.\begin{aligned}kT\log p_1'+\chi_1 = kT\log c_1+\psi_1+c_1\beta_{11}+c_2\beta_{12},\\ kT\log p_2'+\chi_2 = kT\log c_2+\psi_2+c_2\beta_{22}+c_1\beta_{12}.\end{aligned}\right\} \quad (57.6)$$

Subtracting (57.5) from (57.6), and assuming that δp_1 and δp_2 are small, we obtain

$$kT\,\delta p_1/p_1 = c_2\beta_{12} \quad \text{and} \quad kT\,\delta p_2/p_2 = c_1\beta_{12},$$

so that

$$\delta p_1/\delta p_2 = p_1 c_2/p_2 c_1. \quad (57.7)$$

58. Evolution of heat and change of volume in the process of solution

The process of solution is in general accompanied by the evolution or absorption of heat, and we shall now study this effect. As a preliminary we shall determine the minimum work which has to be done to separate the pure solute from solution. The same work is evidently the maximum work which can be obtained in the process of solution.

If the solution process is carried out at constant pressure and temperature, the minimum work is equal to the change of Gibbs free energy. Let us calculate this work for the removal of a very small number δn of solute molecules from the solution. The total change of Gibbs free energy of the system is the sum of the changes for the solution and the pure (i.e. undissolved) solute. For removal of δn molecules of the solute, the change of the Gibbs free energy G of the solution is

$$\delta G = -\frac{\partial G}{\partial n}\delta n = -\mu'\,\delta n,$$

where μ' is the chemical potential of the solute in solution, while the change of the Gibbs free energy G_0' of the pure solute is

$$\delta G_0' = \frac{\delta G_0'}{\partial n}\delta n = \mu_0'\,\delta n,$$

since the amount of pure solute has been increased by δn molecules (μ_0' being the chemical potential of the pure solute). Consequently the minimum work necessary to separate δn molecules from solution at constant pressure and temperature is

$$\delta W = \delta n(\mu_0' - \mu'). \tag{58.1}$$

We now substitute for μ' from (53.6) and obtain

$$\delta W = \delta n(\mu_0' - \psi - kT\log c) = kT\,\delta n \log[c_0(p, T)/c], \tag{58.2}$$

where c is the concentration of the solution and $c_0(p, T)$ is defined by

$$c_0(p, T) = e^{(\mu_0' - \psi)/kT}. \tag{58.3}$$

The quantity $c_0(p, T)$ is evidently the solubility, i.e. the concentration of the saturated solution (the solution which is in equilibrium with the pure solute). This identification follows directly from the fact that for equilibrium between solution and solute W must have a minimum value, i.e. $\delta W = 0$, as has already been pointed out more than once. Equation (58.3) for the solubility can also be obtained

directly from the condition of equilibrium between the solution and the pure solute (i.e. from the equality of the chemical potentials of the solute in solution and in the pure state).

It is important to notice that c_0 can be identified with the concentration of the saturated solution *only* provided that c_0 is small, since the results of the preceding sections are valid only for dilute solutions.

There is now no difficulty in calculating the heat δQ_p which is absorbed when δn molecules are dissolved at constant pressure. If δQ_p is negative, this means that heat is given out instead of being absorbed. Using (17.19) we find at once

$$\delta Q_p = T^2 \frac{\partial}{\partial T}\left(\frac{\delta W}{T}\right) = kT^2 \delta n \frac{\partial \log c_0}{\partial T}. \tag{58.4}$$

We shall now find also the change of volume in the process of solution, i.e. the difference between the sum of the volumes of the pure solute and the solution (or as a special case the pure solvent) in which it is dissolved, and the volume of the solution after the solute has been dissolved.

The volume is the derivative of the Gibbs free energy with respect to pressure, and consequently the change of volume is equal to the derivative (with respect to pressure) of the change of Gibbs free energy in the process of solution, i.e. of the minimum work which has to be done to carry out the reverse process. Thus for the solution of δn molecules the change of volume δV is given by

$$\delta V = \frac{\partial}{\partial p} \delta W, \tag{58.5}$$

where δW is given by (58.2), so

$$\delta V = kT\,\delta n\,\partial \log c_0/\partial p. \tag{58.6}$$

To conclude this section we may point out that the result (58.4) is in agreement with the Le Chatelier-Braun principle. Suppose for instance that δQ_p is negative, i.e. heat is given out in the solution process, and consider a saturated solution. Then if this solution is cooled, the solubility will increase, since in this case dc_0/dT is positive by (58.4); thus more of the solute will dissolve, and this will cause a production of heat which tends to oppose the cooling influence, in accordance with the Le Chatelier-Braun principle. Similar considerations show that (58.6) is also in agreement with the Le Chatelier-Braun principle.

EXAMPLES

1. Find the maximum work which can be done in the formation of a saturated solution.

SOLUTION. Before dissolution the Gibbs free energy of the pure solvent was $N\mu_0$, while that of the solute was $n\mu_0'$, so that the total Gibbs free energy was

$$G_1 = N\mu_0 + n\mu_0'.$$

After dissolution the Gibbs free energy becomes

$$G_2 = N\mu_0 + nkT\log(n/eN) + n\psi.$$

The maximum work is therefore

$$W_{\max} = G_1 - G_2 = -nkT\log(n/eN) + n(\mu_0' - \psi),$$

or, substituting $\mu_0' - \psi = kT\log c_0$ from (58.3),

$$W_{\max} = nkT\log(ec_0/c).$$

If the solution is saturated, $c = c_0$ and $n = Nc = Nc_0$, so

$$W_{\max} = nkT = Nc_0kT.$$

These results can also be obtained by direct integration of (58.2), since

$$\delta n = N\,\delta c.$$

2. Find the minimum work which must be done to increase the concentration of a solution from c_1 to c_2, by removing some of the solvent.

SOLUTION. Before removing the solvent the Gibbs free energy of the solution was

$$G_1 = N\mu_0 + Nc_1kT\log(c_1/e) + Nc_1\psi$$

(N being the initial number of solvent molecules, so that there are Nc_1 solute molecules). In order to increase the concentration to c_2, $N(1 - c_1/c_2)$ solvent molecules have to be removed (so that Nc_1/c_2 are left, for the same number of solute molecules). The sum of the Gibbs free energies of the remaining solution and the solvent which has been removed is

$$G_2 = N\mu_0 + Nc_1kT\log(c_2/e) + Nc_1\psi.$$

Therefore the minimum work required is

$$W = G_2 - G_1 = Nc_1kT\log(c_2/c_1).$$

59. Fluctuations and thermodynamic inequalities for solutions

It was shown in Chapter VI that for a state to exist, certain conditions (the thermodynamic inequalities of § 35) have to be satisfied, and also the fluctuations of the various thermodynamic functions were determined. All these results, however, were obtained for systems consisting of identical particles, and we shall now obtain analogous results for systems with different kinds of particles, limiting ourselves at present to only two species of particles, i.e. to solutions of one substance in another.

The results of § 35 were obtained on the basis of the requirement

that the entropy must be a maximum. If the system is divided up into a number of relatively small parts, then for each of these parts the remaining parts can be considered as the medium surrounding the given part. As the equilibrium condition of a part of the system we used the condition that the minimum work necessary to take the given part out of the equilibrium state into some other state must always be positive (this gave the condition that $E-T_0 S+p_0 V$ must have a minimum, i.e. (35.3)).

We shall here follow a similar procedure. Consider some part of the solution, containing N molecules of the solvent and n molecules of the solute. In the equilibrium state the pressure, temperature, and concentration of this part must have values equal to those of the rest of the solution (i.e. of the 'medium'). Let us determine the minimum work which is necessary to give this part values of the pressure, temperature, and number of solute molecules, differing by small quantities Δp, ΔT, and Δn from their equilibrium values (i.e. the minimum work for a fluctuation), the number N of solvent molecules in this part remaining constant. To do this we apply the considerations of § 35 to the present case.

In order that the minimum work should be done, the process must be carried out reversibly, and then W is equal to the change of energy of the system:

$$W = \Delta E+\Delta E_0$$

(the quantities with a suffix zero refer to the medium, and those without a suffix to the given part). Substituting for ΔE_0 from the thermodynamic identity (43.5), we have

$$W = \Delta E+T_0\Delta S_0-p_0\Delta V_0+\mu_0'\Delta n_0,$$

where μ_0' is the chemical potential of the solute in the 'medium'† (there is no term in the chemical potential of the solvent, since the number of solvent molecules in the given part remains constant in the process). From the reversibility of the process it follows that $\Delta S_0 = -\Delta S$, and from the conservation of the total volume and of the amount of solute it follows that $\Delta V_0 = -\Delta V$ and $\Delta n_0 = -\Delta n$; so we obtain

$$W = \Delta E-T_0\Delta S+p_0\Delta V-\mu_0'\Delta n.$$

Thus the condition of equilibrium must be

$$W = \Delta E-T_0\Delta S+p_0\Delta V-\mu_0'\Delta n > 0. \tag{59.1}$$

Expanding ΔE in powers of ΔV, ΔS, and Δn (considering E as a

† μ_0' should not be confused with the chemical potential of the pure solute.

function of S, V, n, we have (retaining terms up to the second order)

$$\Delta E = \left(\frac{\partial E}{\partial S}\right)_0 \Delta S + \left(\frac{\partial E}{\partial V}\right)_0 \Delta V + \left(\frac{\partial E}{\partial n}\right)_0 \Delta n + \frac{1}{2}\left[\left(\frac{\partial^2 E}{\partial S^2}\right)_0 (\Delta S)^2 + \right.$$
$$+\left(\frac{\partial^2 E}{\partial V^2}\right)_0 (\Delta V)^2 + \left(\frac{\partial^2 E}{\partial n^2}\right)_0 (\Delta n)^2 + 2\left(\frac{\partial^2 E}{\partial V \partial n}\right)_0 \Delta V \Delta n +$$
$$\left. + 2\left(\frac{\partial^2 E}{\partial S \partial n}\right)_0 \Delta S \Delta n + 2\left(\frac{\partial^2 E}{\partial S \partial V}\right)_0 \Delta S \Delta V\right].$$

The suffix zero implies that the derivative must be taken for values of p, T, μ' equal to p_0, T_0, μ'_0. Now we have

$$(\partial E/\partial S)_0 = T_0, \qquad (\partial E/\partial V)_0 = -p_0, \qquad (\partial E/\partial n)_0 = \mu'_0;$$

and we see by substitution into (59.1) that the first-order terms cancel out, and we are left with

$$W = \frac{1}{2}\left[\frac{\partial^2 E}{\partial S^2}(\Delta S)^2 + \frac{\partial^2 E}{\partial V^2}(\Delta V)^2 + \frac{\partial^2 E}{\partial n^2}(\Delta n)^2 + \right.$$
$$\left. + 2\frac{\partial^2 E}{\partial V \partial n}\Delta V \Delta n + 2\frac{\partial^2 E}{\partial S \partial n}\Delta S \Delta n + 2\frac{\partial^2 E}{\partial S \partial V}\Delta S \Delta V\right]. \quad (59.2)$$

In future we shall, as in § 35, omit the suffix zero in quantities which are coefficients of fluctuations, but equilibrium values of these coefficients should always be understood.

From the theory of quadratic forms it is well known that in order that a form with three variables should always be positive (in the present case for all values of ΔS, ΔV, and Δn) its coefficients must satisfy three conditions, which for (59.2) are

$$\begin{vmatrix} \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S \partial V} & \frac{\partial^2 E}{\partial S \partial n} \\ \frac{\partial^2 E}{\partial V \partial S} & \frac{\partial^2 E}{\partial V^2} & \frac{\partial^2 E}{\partial V \partial n} \\ \frac{\partial^2 E}{\partial S \partial n} & \frac{\partial^2 E}{\partial V \partial n} & \frac{\partial^2 E}{\partial n^2} \end{vmatrix} > 0, \qquad \begin{vmatrix} \frac{\partial^2 E}{\partial S^2} & \frac{\partial^2 E}{\partial S \partial V} \\ \frac{\partial^2 E}{\partial V \partial S} & \frac{\partial^2 E}{\partial V^2} \end{vmatrix} > 0, \qquad \frac{\partial^2 E}{\partial S^2} > 0. \quad (59.3)$$

Substituting for the derivatives of E, these conditions become

$$\begin{vmatrix} \frac{\partial T}{\partial S} & \frac{\partial T}{\partial V} & \frac{\partial T}{\partial n} \\ -\frac{\partial p}{\partial S} & -\frac{\partial p}{\partial V} & -\frac{\partial p}{\partial n} \\ \frac{\partial \mu'}{\partial S} & \frac{\partial \mu'}{\partial V} & \frac{\partial \mu'}{\partial n} \end{vmatrix} > 0, \qquad \begin{vmatrix} \frac{\partial T}{\partial S} & \frac{\partial T}{\partial V} \\ -\frac{\partial p}{\partial S} & -\frac{\partial p}{\partial V} \end{vmatrix} > 0, \qquad \frac{\partial T}{\partial S} > 0.$$

Each derivative is taken for constant values of the other two of the variables S, V, n. These determinants can be expressed as Jacobians

$$\frac{\partial(T,p,\mu')}{\partial(S,V,n)} < 0, \qquad \left(\frac{\partial(T,p)}{\partial(S,V)}\right)_n < 0, \qquad \left(\frac{\partial T}{\partial S}\right)_{V,n} > 0. \qquad (59.4)$$

The second and third of these conditions reduce to the inequalities found earlier, i.e. $(\partial p/\partial V)_T < 0$ and $c_v > 0$ (see (35.7, 8)). The first condition can be transformed in the following way:

$$\frac{\partial(T,p,\mu')}{\partial(S,V,n)} = \frac{\partial(T,p,\mu')}{\partial(T,p,n)} \Big/ \frac{\partial(S,V,n)}{\partial(T,p,n)} = \left(\frac{\partial \mu'}{\partial n}\right)_{p,T} \Big/ \left(\frac{\partial(S,V)}{\partial(T,p)}\right)_n < 0.$$

Since by the second condition of (59.4) the denominator of the last fraction is negative, we must have

$$(\partial\mu'/\partial n)_{p,T} > 0, \qquad (59.5)$$

or, introducing the concentration $c = n/N$, instead of n, this becomes

$$(\partial\mu'/\partial c)_{p,T} > 0, \qquad (59.6)$$

since N is constant. Thus in addition to the inequalities (35.7, 8) the inequality (59.6) must also be satisfied in the case of solutions.

Another well-known result from the theory of quadratic forms is that if the quadratic form is essentially positive, as in (59.2), then the last two inequalities of (59.4) cannot become equalities unless the first one also becomes an equality. On the other hand, the first condition may become an equality without the other two doing the same.

If the first condition of (59.4) does become an equality, so that we have

$$(\partial\mu'/\partial c)_{p,T} = 0, \qquad (59.7)$$

then, as we shall show below, a necessary condition for equilibrium is that

$$(\partial^2\mu'/\partial c^2)_{p,T} = 0 \qquad (59.8)$$

should also be satisfied.

If the third-rank determinant of the coefficients of the quadratic form of three variables (i.e. the first of the Jacobians in (59.4)) vanishes, then the theory of these forms shows that the form is actually one with only two independent variables. Consequently in this case it is possible to have fluctuations for which (59.2) is zero; for this to happen it is necessary that only that variable which does not enter into the quadratic form should undergo fluctuations from its equilibrium value. If, however, (59.2) can become an equality, it is necessary to investigate the higher order terms in (59.1) in order to find the conditions for the inequality (59.1) still to hold.

First of all we rewrite the quadratic form (59.2) as

$$W = \tfrac{1}{2}\{\Delta S\Delta(\partial E/\partial S)_{V,n}+\Delta V\Delta(\partial E/\partial V)_{S,n}+\Delta n\Delta(\partial E/\partial n)_{S,V}\}$$
$$= \tfrac{1}{2}(\Delta S\Delta T-\Delta V\Delta p+\Delta n\Delta\mu'), \tag{59.9}$$

and we must investigate the case where this expression vanishes. Since, however, $(\partial\mu'/\partial n) = 0$, we must have $\Delta\mu' = (\partial\mu'/\partial T)\Delta T+(\partial\mu'/\partial p)\Delta p$, and so if ΔT and Δp are both zero, $\Delta\mu'$ must also be zero, and consequently (59.9) must also vanish. Thus in order to investigate the case when (59.9) vanishes it is sufficient to consider fluctuations in which $\Delta T = 0$ and $\Delta p = 0$, i.e. fluctuations at constant temperature and pressure. For such fluctuations (59.1) becomes

$$\Delta G-\mu_0'\Delta n > 0.$$

Expanding ΔG in powers of Δn and remembering that $\partial G/\partial n = \mu'$ we find

$$\frac{1}{2}\frac{\partial\mu'}{\partial n}(\Delta n)^2+\frac{1}{6}\frac{\partial^2\mu'}{\partial n^2}(\Delta n)^3+\frac{1}{24}\frac{\partial^3\mu'}{\partial n^3}(\Delta n)^4+\ldots > 0$$

(all the derivatives are for constant p and T). If (59.7) is true, i.e. $\partial\mu'/\partial n = 0$, we see that this inequality can be fulfilled only if the coefficient of $(\Delta n)^3$ vanishes, i.e. if (59.8) is true, and, moreover, the coefficient of $(\Delta n)^4$ must be positive, which gives

$$(\partial^3\mu'/\partial c^3)_{p,T} > 0. \tag{59.10}$$

States determined by the two equations (59.7, 8) of the three variables p, T, c can be represented by curves which show the relation between two of the variables for given values of the third. These curves are known as 'critical lines'.

We shall now investigate the fluctuations in solutions. By the general formula (40.1) the probability of a fluctuation is

$$w \propto e^{-W/kT}.$$

For W we may use the expression (59.9), and making the substitutions

$$S = -\partial G/\partial T = -G_T, \quad V = \partial G/\partial p = G_p, \quad \mu' = \partial G/\partial n = G_n$$

(where a suffix denotes a derivative with respect to the variable indicated), we obtain

$$W = \tfrac{1}{2}(-\Delta T\Delta G_T-\Delta p\Delta G_p+\Delta n\Delta G_n).$$

Expanding ΔG_T in the form

$$\Delta G_T = G_{TT}\,\Delta T+G_{Tp}\,\Delta p+G_{Tn}\,\Delta n$$

(and similarly for ΔG_p and ΔG_n), and substituting into W, we find

$$W = \tfrac{1}{2}\{-G_{TT}(\Delta T)^2-2G_{Tp}\,\Delta p\Delta T-G_{pp}(\Delta p)^2+G_{nn}(\Delta n)^2\}.$$

Substituting this expression for W into $w \propto e^{-W/kT}$, and putting in the values of the various second derivatives of G, we finally obtain

$$w \propto \exp\left\{-\frac{C_v}{2kT^2}(\Delta T)^2+\frac{(\partial V/\partial T)_{p,n}}{kT}\Delta T\Delta p+ \right.$$
$$\left. +\frac{(\partial V/\partial p)_{T,n}}{2kT}(\Delta p)^2-\frac{(\partial \mu'/\partial n)_{p,T}}{2kT}(\Delta n)^2\right\}. \quad (59.11)$$

This expression splits up into the product of two factors, one depending on ΔT and Δp and the other only on Δn. Hence we see that the fluctuation of the number of particles n or of the concentration $c = n/N$ (since N is constant) is independent of the fluctuations of pressure and temperature, i.e.

$$\overline{\Delta T\Delta c} = 0, \qquad \overline{\Delta p\Delta c} = 0. \quad (59.12)$$

Comparing the factor containing $(\Delta n)^2$ in (59.11) with the general formula (38.3) for the Gaussian distribution we find for the fluctuation of the number of dissolved particles

$$\overline{(\Delta n)^2} = kT/(\partial \mu'/\partial n)_{p,T},$$

or dividing by N^2,

$$\overline{(\Delta c)^2} = kT/N(\partial \mu'/\partial c)_{p,T}. \quad (59.13)$$

The expressions for $\overline{(\Delta T)^2}$ and $\overline{(\Delta p)^2}$ and $\overline{\Delta T\Delta p}$ are the same as those already obtained in § 40. On the critical line $(\partial \mu'/\partial c)_{p,T} = 0$ and so we see that $\overline{(\Delta c)^2}$ becomes infinite.

EXAMPLE

Determine $\overline{(\Delta c)^2}$ for a dilute solution.

SOLUTION. Substituting $\mu' = kT\log c+\psi(p, T)$ into (59.13) we find

$$\overline{(\Delta c)^2} = c/N.$$

60. Vapour pressure of a solution

We shall now investigate the equilibrium of a solution with its vapour, the latter in general containing molecules both of the solvent and the solute. The solution will no longer be assumed dilute, i.e. the relative numbers of molecules of the two species may be arbitrary (it should be remembered that the results of § 55 referred only to dilute solutions).

Since the solution and its vapour are in equilibrium, the chemical potentials μ_1 and μ_2 of the two components in the solution and in the vapour must be equal to each other. If we denote the numbers of

particles of the two species which are in the solution by $N_{1\,\mathrm{sol}}$ and $N_{2\,\mathrm{sol}}$, then for the solution the identity (46.9) can be written as

$$d\Omega = -N_{1\,\mathrm{sol}}\,d\mu_1 - N_{2\,\mathrm{sol}}\,d\mu_2 - S_{\mathrm{sol}}\,dT - p\,dV_{\mathrm{sol}}, \qquad (60.1)$$

where S_{sol} and V_{sol} are the entropy and volume of the solution (the temperature T and pressure p are the same for the solution and vapour).

We shall assume that the vapour is sufficiently rarified to be considered as a perfect gas, i.e. that the vapour pressure is very low. On this assumption we shall neglect the terms proportional to p in (60.1), i.e. $p\,dV$ and $d\Omega$ (since $\Omega = -pV$). Moreover, we shall consider all the differentials to be at constant temperature, so that (60.1) becomes

$$N_{1\,\mathrm{sol}}\,d\mu_1 + N_{2\,\mathrm{sol}}\,d\mu_2 = 0. \qquad (60.2)$$

At the same time, for the gaseous phase we have from (30.5)

$$\mu_1 = kT\log p_1 + \chi_1(T),$$
$$\mu_2 = kT\log p_2 + \chi_2(T),$$

where p_1 and p_2 are the partial pressures of the two components in the vapour. Differentiating μ_1 and μ_2 (for constant T) we obtain

$$\left.\begin{aligned} d\mu_1 &= kT\,d\log p_1,\\ d\mu_2 &= kT\,d\log p_2,\end{aligned}\right\} \qquad (60.3)$$

and substituting these expressions into (60.2) we obtain

$$kT(N_{1\,\mathrm{sol}}\,d\log p_1 + N_{2\,\mathrm{sol}}\,d\log p_2) = 0. \qquad (60.4)$$

Let ξ be the concentration of the solution, defined as the ratio of the number of particles of the first species to the total number in solution, i.e.

$$\xi = N_{1\,\mathrm{sol}}/(N_{1\,\mathrm{sol}}+N_{2\,\mathrm{sol}});$$

then evidently

$$1-\xi = N_{2\,\mathrm{sol}}/(N_{1\,\mathrm{sol}}+N_{2\,\mathrm{sol}}).$$

Similarly, let x be the concentration of the vapour defined in an analogous manner. The partial vapour pressures p_1 and p_2 are equal to the products of the total pressure and the concentrations of the two components (see § 30), so that

$$p_1 = xp, \qquad p_2 = (1-x)p.$$

Substituting this into (60.2) and dividing by the total number of particles in solution, $N = N_{1\,\mathrm{sol}}+N_{2\,\mathrm{sol}}$, we find

$$kT[\xi\,d\log px + (1-\xi)\,d\log p(1-x)] = 0.$$

Hence

$$d\log p = \frac{(x-\xi)}{x(1-x)}\,dx, \qquad (60.5)$$

from which it follows that

$$\xi = x - x(1-x)\partial \log p/\partial x. \tag{60.6}$$

This equation gives the relation between the concentration of the solution and the concentration of its vapour.

61. Equilibrium curves

The state of bodies consisting of identical particles is in general determined by the values of any two variables such as p and T. For systems with two components (*binary mixtures*), however, the values of three variables must be known to determine the state: for instance p, T and the concentration x of the mixture (the concentration is defined here, and subsequently, as the ratio of the number of molecules of one of the components to the total number of molecules, and evidently x can vary from 0 to 1). Consequently the state of a binary mixture can be represented by a point in a three-dimensional space, where the coordinate axes represent the three variables (just as the state of a system with only one component could be represented by a point in a plane).

According to the phase rule (§ 52) a two-component system cannot contain more than four phases simultaneously in contact. Moreover, the number of thermodynamic degrees of freedom will be two for two phases, one for three phases, and zero for four phases. Thus states in which two phases coexist in equilibrium are represented by points lying on a surface in the three-dimensional space, states with three phases in equilibrium by points on a line (known as the line of triple points or the three-phase line), and states with four phases in equilibrium by isolated points.

It will be remembered that in the case of a one-component system, states with two phases in equilibrium could be represented by a curve in the p, T diagram for instance, each point of this curve giving the values of p and T for the two phases (these values being the same in the two phases, by the phase equilibrium condition). The points on either side of the curve then represent uniform states of the substance. If, however, the states are represented on a volume-temperature diagram, the phase equilibrium is represented by a curve within which the points correspond to phase separation, and the states of the two phases are given by the intersection of lines T = const. with the curve.

Similar considerations apply also for binary mixtures. If the axes

of coordinates are p, T and the chemical potential μ of one of the components (i.e. variables which have the same values in contiguous phases), then equilibrium of the two phases is represented by a surface, each point of which determines p, T and μ for the two phases in equilibrium. If there are three phases, the points representing their equilibrium (triple points) will lie on the curves of intersection of the equilibrium surfaces for any two of the phases.

However, the use of the variables p, T, μ is inconvenient, and in future we shall use the quantities p, T, x as independent variables. In terms of these variables the equilibrium of two phases is represented by a surface, whose points of intersection with the straight line p = const., T = const. represent equilibrium states of the two phases for given p and T (i.e. determine the concentrations, which may, however, be different in the two phases). Points on the straight line (p = const., T = const.) between two points of intersection with the equilibrium surface, represent states in which the body would be unstable if it remained uniform, and consequently these are states for which separation into the two phases takes place (the concentrations of the two phases being given by the intersections with the surface). Since the surface represents equilibrium of two phases with each other, evidently it must be such that the number of its intersections with a straight line parallel to the x-axis is in general even.

In what follows we shall generally use only two-dimensional diagrams, the axes of coordinates being either p and x or T and x; and in these diagrams we can show the intersections of the equilibrium surface with planes of constant temperature or constant pressure respectively. The curves thus obtained we shall call *equilibrium curves.*

Consider a point on an equilibrium curve for which the concentrations in both phases become equal; there are then two possible cases: (1) that all the other properties of the two phases become equal at this point, i.e. the phases become identical, or (2) the two phases remain different at this point. In the former case the point is called a *critical point*, and in the latter a *point of equal concentrations.*

In the neighbourhood of a critical point the equilibrium curve must have a form like that shown in Fig. 12, or a similar one with K a minimum instead of a maximum. The axis of abscissae represents x, and the axis of ordinates represents either p or T, so that the curve is the intersection of the equilibrium surface with either a plane of

constant temperature or one of constant pressure (only a part of the equilibrium curve is shown in the diagram). Points in the shaded area inside this curve represent unstable states in which separation into the two phases occurs, the resulting concentrations of the two phases being given by the intersections of the curve and the appropriate horizontal line. At the point K the two phases become identical, as can be seen from the fact that the transition between the two points coinciding at K can be carried out along any infinitely short path outside the shaded area without any separation into phases.

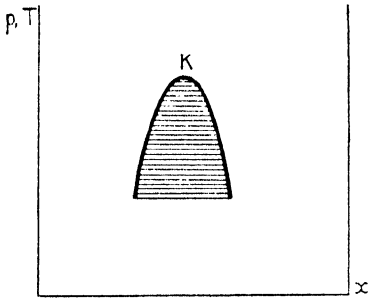


FIG. 12.

As can be seen from Fig. 12, it is possible to find states in the neighbourhood of the critical point for which the two phases can be in equilibrium with arbitrarily close values of the concentration, say x and $x+dx$ respectively. The equilibrium condition for these states is

$$\mu(p, T, x) = \mu(p, T, x+dx),$$

where μ is the chemical potential of one of the components of the mixture. Hence we see that at a critical point we must have

$$(\partial\mu/\partial x)_{p,T} = 0. \tag{61.1}$$

This condition is identical with the condition (59.7), and so the two definitions of a critical point (here and in § 59) are equivalent. It should be noticed that μ in (61.1) is the chemical potential of either of the components, but the condition obtained by taking the chemical potential of the other component is easily seen to be equivalent, if we remember that each of the chemical potentials is the derivative of G with respect to the corresponding number of particles.

The critical points evidently lie on some curve (the critical line) on the equilibrium surface, as can be seen from the fact that they are defined by one additional condition (61.1) on the equilibrium surface (this has already been pointed out in § 59).

In the neighbourhood of a point of equal concentrations the equilibrium curves must have a form like that shown in Fig. 13 (or the analogous curve with K a minimum), with two curves touching at the maximum (or minimum) point. The shaded region between

the two curves is the region of phase separation. At the point K the concentrations of the two phases for which the phases are in equilibrium become equal, but the phases nevertheless continue to have a separate identity, for in order to go from one of the points coincident at K to the other, it is necessary to cross the shaded region of

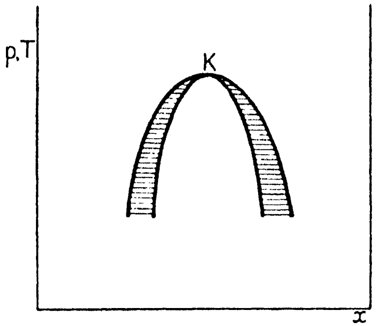


FIG. 13.

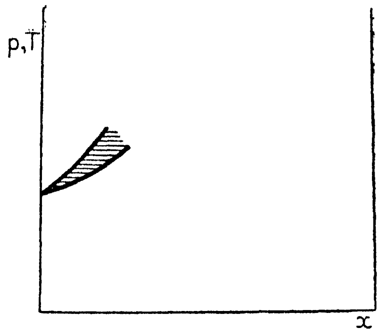


FIG. 14.

separation into two phases. Just as in the case of critical points, the points of equal concentration lie on some curve in the equilibrium surface.

We shall now discuss the properties of equilibrium curves for small concentrations, i.e. when there is much less of one component in the mixture than the other. The intersection of the equilibrium surface with the plane $x = 0$ (or $x = 1$) is just the phase equilibrium curve of one of the pure components. It was shown in § 55 ((55.5) and (55.7)) that for small concentrations (all the results of § 55 refer to dilute solutions) the difference between the temperatures of phase equilibrium of the solution and the pure solvent (at given pressure) was proportional to the difference of the concentrations in the two phases, the same being true for the difference of pressures at a given temperature. Moreover, in § 56 it was shown (again for small concentrations) that the ratio of concentrations in the two phases depends only on p and T, so that it can be considered as constant in the neighbourhood of $x = 0$.

From these considerations it follows that the equilibrium curves have the form shown in Fig. 14, i.e. for small concentrations they are two straight lines intersecting at $x = 0$ (directed either upwards or downwards). The same is evidently true for concentrations close to unity. The region between the two straight lines is that of phase

separation, while the regions above and below are the regions of one or the other phase separately.

At the beginning of this section we pointed out that systems of two components may consist of three phases in contact. If the states are represented by points in a three-dimensional space, with p, T and the chemical potential of one of the components as axes, then the states with three phases will be represented by triple points lying on the curves of intersection of the equilibrium surfaces for each two of the three phases. If the axes are p, T and x, the triple points will again lie on the three curves of intersection of the equilibrium surfaces of the first and second phases, the second and third phases, and the third and first phases. Each equilibrium state of the three phases with each other will then be represented by three points simultaneously, one on each of the three intersection curves. Consider now the intersection of the three equilibrium surfaces with a plane of constant pressure or temperature. Near a triple point the equilibrium curves will have the appearance shown in Fig. 15. Since all three phases must have equal pressures and temperatures in equilibrium, the three points A, B, C must lie on a straight line parallel to the x-axis. The point A which, say, determines the concentration of the first phase at the triple point is the point of intersection of the equilibrium curves 12 and 13, for the first and second and for the first and third phases respectively. Similarly, the point B is the intersection of 12 and 23, the curves for the first and second, and second and third phases respectively, and C is the intersection of 23 and 13, the curves for the second and third, and first and third phases respectively. The points A, B, C are also of course the points of intersection of the plane p = const. or T = const. with the three curves of intersection of the equilibrium surfaces. Of these curves we shall give the name *line of triple points* or *three-phase line* to the one corresponding to B in Fig. 15. The points in regions I, II, and III represent states of the first, second, and third phases separately. The region between the curves 13 and below the straight line ABC

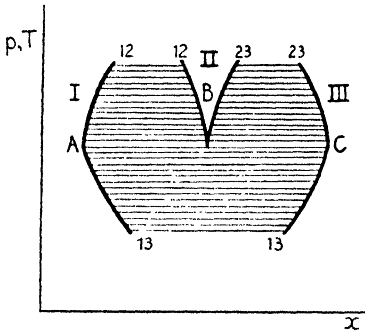


Fig. 15.

corresponds to phase separation into the first and third phases, that between the curves 12 above ABC corresponds to phase separation into the first and second phases, and that between the curves 23 above ABC to phase separation into the second and third phases. Evidently the region II must be situated entirely above ABC (or entirely below ABC). At the points A, B, C the curves 12, 13, and 23 generally speaking intersect at some angle and do not go over into each other

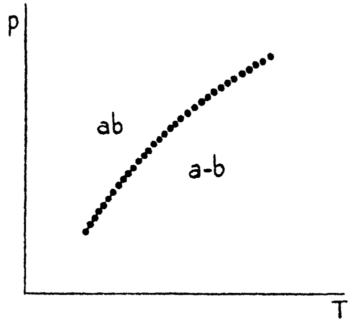


Fig. 16.

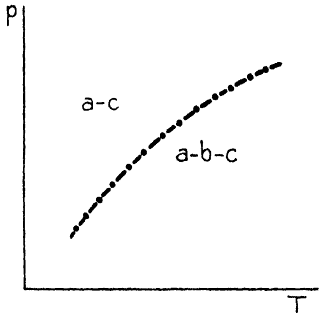


Fig. 17.

continuously. The directions of 12, 13, 23 need not of course necessarily be as shown in Fig. 15, the only essential feature being that the curves 12 and 23 and the curve 13 must lie on opposite sides of ABC.

If we project one of the special lines in the equilibrium surfaces on to the p, T plane, the projection will divide this plane into two parts. In the case of a critical line, the points representing separation into two phases will be projected into one of these parts, while the points corresponding to uniform states (with no phase separation) will be projected into the other part. The projection of the critical line on the p, T plane is shown by the dotted line in Fig. 16; *a* and *b* denote the two phases, *a–b* denotes the states of *a* and *b* separately and the states with *a* and *b* in equilibrium together, while *ab* denotes the single phase in which there is no distinction between the two phases (above the critical point).

Similarly, the projection of the three-phase line also divides the p, T plane into two parts, and Fig. 17 shows how the various points are projected (the symbol *a–b–c* denotes that the points are projections of points representing states of the three phases *a*, *b*, *c*, separately, and states in which phase separation into *a* and *b* or *b* and *c* takes place).

In a similar way Fig. 18 shows the projection of the line of points of equal concentration, and Fig. 19 shows the phase equilibrium curve of the pure component (i.e. the intersection of the equilibrium surface with the plane $x = 0$). The symbol b in Fig. 19 means that on that part of the p, T plane the points are projections of points representing states in phase b alone. It should be noticed that the order of the letters in the symbols a–b, a–b–c is such that b denotes a

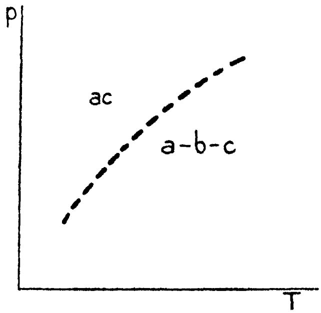


FIG. 18.

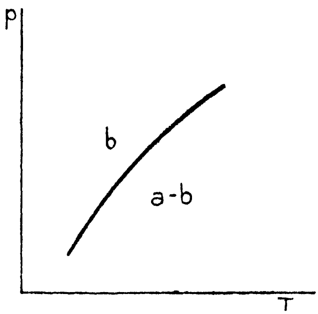


FIG. 19.

phase of concentration larger than a, and c of concentration larger than b.

We may notice also that the four types of special points in the equilibrium curves (i.e. the triple point, the point of equal concentrations, the critical point, and the point $x = 0$) represent four possible types of maximum (or minimum) of these curves.

If one of the phases always has the same composition (i.e. concentration) independently of the values of p and T, then the equilibrium curves in the neighbourhood of the special points considered above assume a rather different form. One example of this kind of phase is a chemical compound of the two components, and another is the phase of a pure component, i.e. a phase always having concentration $x = 0$ (or $x = 1$).

We shall now examine the form of the equilibrium curves, in the presence of a phase of constant composition, close to the point in which the line corresponding to this phase terminates. It is evident that this point must be either a maximum or minimum of the equilibrium curve, and hence must belong to one of the types discussed in this section.

If the phase of constant composition is a phase of the pure com-

ponent (concentration $x = 0$), then the corresponding line must coincide with the axis of p or T, and may terminate in a point of the type shown in Fig. 14. Close to this point the equilibrium curve has the form shown in Fig. 20, i.e. one of the straight lines in Fig. 14 here coincides with the axis of ordinates.

If one of the phases is a chemical compound of definite composition,

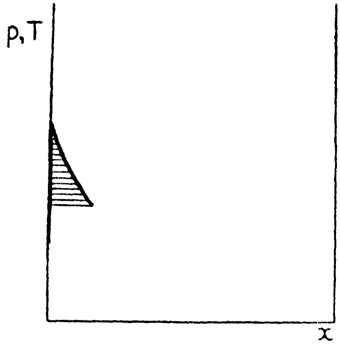


FIG. 20.

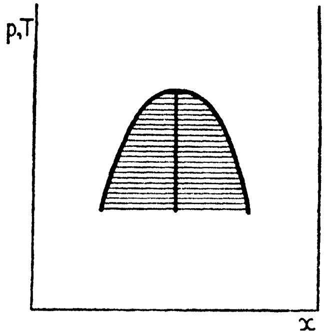


FIG. 21.

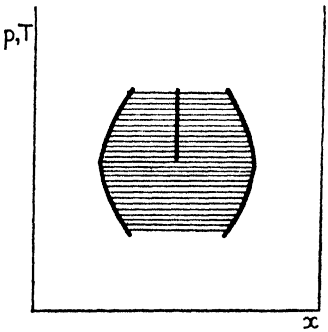


FIG. 22.

then near the point of equal concentrations the equilibrium curve will have a form like that shown in Fig. 21, i.e. the internal region in Fig. 13 collapses to a vertical line. The shaded region on either side of this line is the region of separation into two phases, one of which is the chemical compound, whose concentration is given by this line. Similarly, near the triple point the equilibrium curve assumes a form like that shown in Fig. 22. The chemical compound phase is represented by the vertical line, into which the region II of Fig. 15 collapses in this case.

62. Examples of equilibrium diagrams

We shall now enumerate the main types of equilibrium curves, and, in contrast to the preceding section, we shall examine these not only in the neighbourhood of special points, but over the whole range of concentrations. These curves (also called equilibrium diagrams) may have a great variety of forms, but in the majority of cases they can be considered as falling into one of the types we shall enumerate below, or else as a combination of more than one of these types. The shaded regions in all these diagrams will always represent the regions of phase separation, and the unshaded regions correspond to uniform states. The points of intersection of horizontal lines with the curves bounding the regions of phase separation give the concentrations of the phases into which the separation takes place (at given p and T).

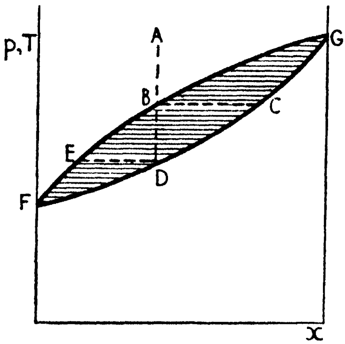


FIG. 23.

(1) There are two phases, each of which can have any value of the concentration (i.e. the two components will mix in any proportion in either phase). In the simplest case, where the curves have no maximum or minimum (apart from the points corresponding to the pure components), the equilibrium diagram has a form like that shown in Fig. 23 (often called the 'cigar' type). Suppose for instance that one of the phases is a liquid (the region above the cigar in the T, x diagram), and the other is a solid solution (the region below the cigar). If the liquid mixture is cooled at given concentration, then at the temperature given by the intersection B of the vertical line AD (corresponding to the given concentration) and the upper curve of the cigar, the liquid begins to solidify. The solid that separates out will be a solid solution of concentration C, i.e. with a bigger concentration than the liquid. This will consequently reduce the concentration of the remaining liquid, so that its freezing-point will be lowered (thus as it were opposing further solidification, in agreement with the Le Chatelier-Braun principle). For further reduction of temperature the point representing the state of the liquid phase will move down along the upper curve, and the point representing the solid solution will move down the lower curve. If the solid solution

remains all the time in contact (i.e. in equilibrium) with the liquid, then it is evident that the liquid will have completely solidified at the temperature for which the solid solution has the same concentration as the initial concentration of the liquid (i.e. at the temperature corresponding to E). Thus the beginning and end of the solidification take place at temperatures given by the intersections of the vertical line AD, with the upper and lower curves respectively. If, however,

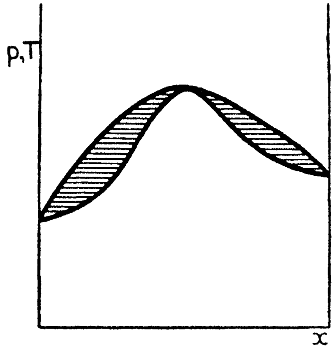


FIG. 24.

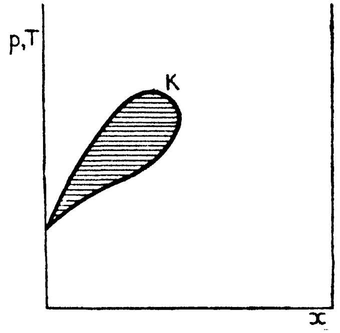


FIG. 25.

the phase which separates out is continually removed (as for instance the vapour over a liquid boiling in an open vessel), then the complete transition into the other phase ends at the temperature for phase equilibrium of one of the pure components (the point F or G in Fig. 23).

Quite analogous considerations apply if the two phases are liquid and gas, or solid and gas. In the former case, the upper curve of the cigar is called the condensation curve, and the lower the boiling curve.

(2) If, as in (1), the two components can be mixed in arbitrary proportions in either phase, but there is a point of equal concentrations, then the equilibrium curve has the appearance shown in Fig. 24 (or a similar diagram with a minimum). At the point of equal concentrations the two curves touch each other and have either a maximum or a minimum.

(3) Two phases, liquid and gas (in each of which the two components can mix in arbitrary proportions), with a critical point. The equilibrium diagram is shown in Fig. 25 (K is the critical point). The region below the curve (in the T, x diagram) corresponds to the liquid phase (or to the gaseous phase in the p, x diagram), and correspondingly the region above the curve represents the gas (or in the p, x

diagram, the liquid). Above the point K there is only phase (so that we can no longer speak of gas or liquid). It is possible to have the analogous diagram with K a minimum, and also to have a diagram with two critical points, one a maximum and one a minimum, so that the region of phase separation (into two solutions) is bounded by a closed curve.

(4) The two components cannot mix in all proportions (for instance

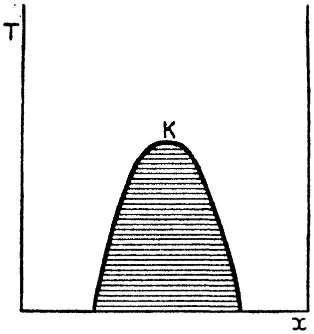


FIG. 26.

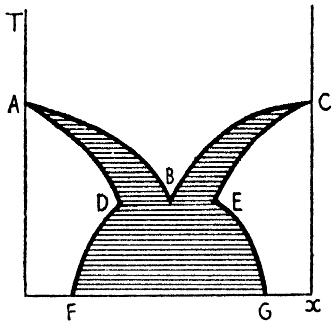


FIG. 27.

two liquids which do not mix in all proportions). The equilibrium diagram is shown in Fig. 26. At temperatures above the critical point K the components can mix in any proportions; below this temperature the components cannot mix in proportions represented by points in the shaded area. Inside this area the substance separates into two liquid mixtures, whose concentrations are given by the intersection of the appropriate horizontal line with the equilibrium curve.

(5) The components in the liquid (or gaseous) phase can mix in any proportions, but for the solid (or liquid) phase they *cannot* mix in all proportions (limited miscibility). In this case there is a triple point. According as the triple point temperature is lower than the phase equilibrium temperatures of the pure components (A and C), or lies between them (it evidently cannot be higher than both A and C, under our assumption that the components can mix in any proportions in the higher temperature phase), the equilibrium diagram will be like Fig. 27 or like Fig. 28. Suppose for instance that the phase of unlimited solubility is the liquid, and that of limited solubility the solid. The region above ABC (Fig. 27) or above ADC (Fig. 28) is then that of liquid states, and the regions on the sides of

ADF and *CEG* (Fig. 27) or *ABF* and *CEG* (Fig. 28) those of solid phases. At the triple point (whose temperature is that of the horizontal line *DBE*) the liquid and two solid phases are in equilibrium together. The point *B* in Fig. 27 is called the *eutectic point*. The liquid mixture with the concentration corresponding to this point solidifies as a whole at this concentration (while for other concentrations the solid that separates out has a concentration different from that of

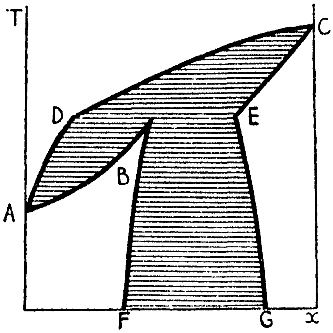


FIG. 28.

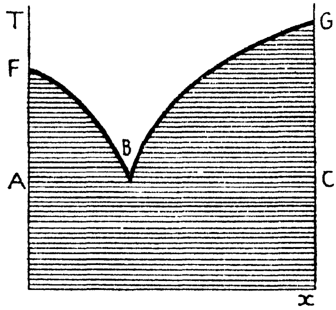


FIG. 29.

the liquid). The regions *ADB* and *CBE* (Fig. 27) or *ADB* and *CDE* (Fig. 28) are those of separation into a liquid and one of the solid phases, while *DEFG* (Fig. 27) or *BEFG* (Fig. 28) are regions of separation into two solid phases.

If in the case of a diagram of the type of Fig. 27 the components cannot mix at all in one of the phases (i.e. one of the phases is that of a pure component), the equilibrium diagram assumes the form shown in Fig. 29 (see end of § 61). In the shaded regions above *ABC* we have the mixed phase in equilibrium with one of the pure components, while below *ABC* the two pure components exist together without mixing. If for instance the upper phase is the liquid mixture, and the lower phase is the solid one, then on lowering the temperature of the liquid one or other of the pure components will separate out, according as the concentration of the liquid lies to the left or the right of the eutectic point. For further lowering of temperature the concentration of the liquid will vary along the curve *FB* or *GB*, and the liquid will solidify as a whole at the eutectic point.

(6) In the phase corresponding to a higher temperature (for instance the liquid) the two components have unlimited solubility, while in the other (the solid) the two components do not mix at all,

but can combine to form a chemical compound of definite composition (Fig. 30). The vertical line DEF gives the composition of the chemical compound. There are now two triple points B and G for which the liquid phase, the solid chemical compound, and one of the pure components can be in equilibrium together. The point D

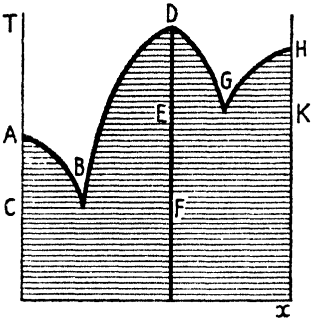


FIG. 30.

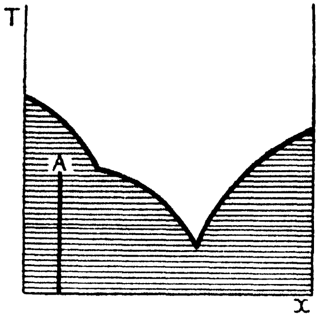


FIG. 31.

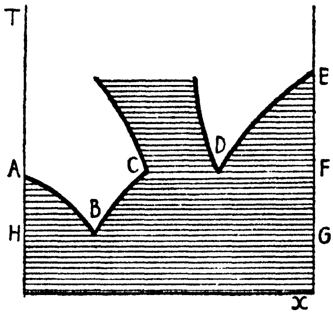


FIG. 32.

between B and G is the point of equal concentrations (see § 61, Fig. 21). It is easily seen where and how separation into phases occurs (in the region DBF into the liquid and the solid compound, below CF into one of the pure component solids and the solid compound, and so on). The solidification of the liquid becomes complete at one of the eutectic points B or G, according as to whether the initial concentration of the liquid lies to the left or to the right of DEF.

(7) In one of the phases (that of the higher temperature) the components have unlimited solubility, while in the other the components do not mix at all, but can combine to form a chemical compound, which is, however, stable only up to a certain temperature

(so that it cannot exist above this temperature). In this case the vertical line corresponding to the compound may not be able to end in a point of equal concentrations, as in Fig. 30, if the temperature of the phase boundary curve is too high. Consequently it may end in a triple point of the type shown in Fig. 22, § 61 (the point A in Fig. 31). The nature of the phase separation in the various parts of the shaded area of Fig. 31 can be easily deduced.

(8) In the phase corresponding to the lower temperature (e.g. the solid phase) the components do not mix at all, while in the other phase (the liquid) they have a limited solubility. In this case (Fig. 32) there are two triple points, in one of which (B) the liquid and the two pure solid components are in equilibrium, and in the other (D) two mixed liquid phases of different concentrations and one of the pure components (solid). The unshaded areas above ABC and DE represent liquid states of different concentrations, the shaded area above CD represents the various separations into the two liquid phases, the shaded area $CFGB$ represents separation into a liquid and one of the pure solid components and so on.

63. The intersections of the special lines on the equilibrium surface

The four kinds of curves considered in § 61 (i.e. critical lines, three-phase lines, lines of equal concentrations, and phase equilibrium curves of a pure component) all lie on a common surface (the equilibrium surface), and so they may in general intersect each other. In this section we shall enumerate some of the properties of the points of intersection of these curves. Most of these properties follow directly from the general properties of equilibrium curves discussed in § 61, but we shall not give any proofs.

We shall show in schematic diagrams the projections of the lines concerned on to the p, T plane (see § 61); the projection of a critical line will be represented by a dotted line, that of the phase equilibrium curve of a pure component by a full line, that of a line of equal concentrations by a broken line, and finally that of a three-phase line by a line of dots and dashes.

First of all it can be shown that two critical lines or two lines of equal concentration can never intersect.

The critical line and the phase equilibrium curve of a pure component terminate at their point of intersection (Fig. 33). The same

is true of the critical line and the three-phase line (Fig. 34), and in both cases the lines meet at an acute angle.

At the intersection of the phase equilibrium curve of a pure com-

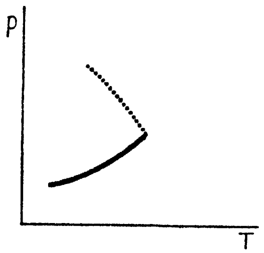


Fig. 33.

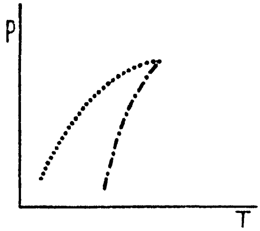


Fig. 34.

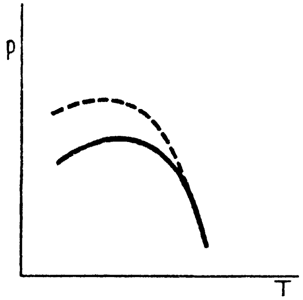


Fig. 35.

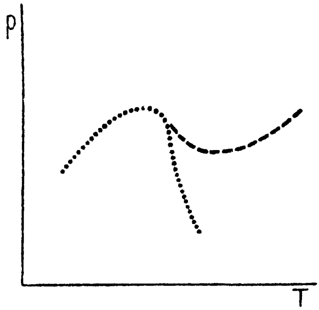


Fig. 36.

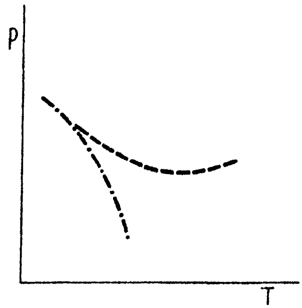


Fig. 37.

ponent and the line of equal concentrations only the latter terminates (Fig. 35), and the two curves touch each other at the point of intersection. The same is true of the intersection of the line of equal concentrations with the critical line (Fig. 36) and with the three-phase line (Fig. 37). In both these cases it is the line of equal con-

centrations which terminates and touches the other curve at the point of intersection.

The point of intersection of the three-phase lines (Fig. 38) is *the quadruple point*, i.e. the point of equilibrium of four phases with each other. At the point of intersection the four three-phase lines meet, corresponding to equilibrium between each three of the four phases.

Finally it is evident that three phase equilibrium curves of the

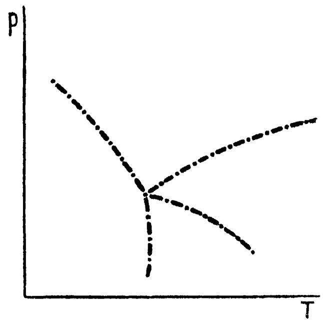


FIG. 38.

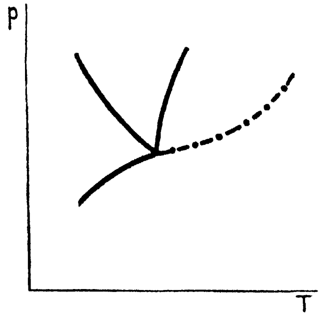


FIG. 39.

pure component (i.e. corresponding to equilibrium between each pair of the three phases of this component) meet at a point lying on a three-phase line (Fig. 39).

64. Gas and liquid

We shall now examine in somewhat greater detail the two-component system with two phases, one of which is liquid and the other gaseous. In the gaseous phase it is obvious that all substances can mix in arbitrary proportions; in the liquid phase, however, some substances can mix in any proportions, but others will not (liquids with limited miscibility).

In the first case, i.e. if the two components can mix in any proportions in either phase, the equilibrium diagram can have no triple points, since the system cannot consist of more than two phases (since all the liquid states belong to one phase, and similarly for the gaseous states). Consider the projection on the p, T plane of the special lines in the equilibrium surface. There are two phase equilibrium curves of the pure components, i.e. for concentrations $x = 0$ or $x = 1$ in both phases. One of these curves already lies on the p, T plane, while the other lies on a parallel plane so that its projection is identical with itself. Each of these curves terminates at some

point (A and B in Fig. 40), which is the critical point for the phases of the corresponding pure substance, and these points are also the end points of the critical line (since the critical line terminates at its intersection with the phase equilibrium curve of a pure component (see § 63)). Thus the projections of the various lines on the p, T plane have the appearance shown in Fig. 40 (the symbolism is the same as that in §§ 61, 63, and l and g refer to liquid and gas phases, in the

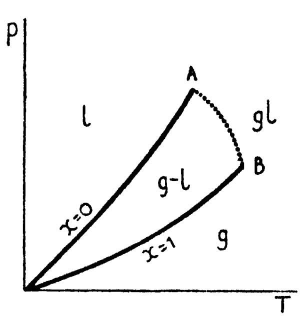


FIG. 40.

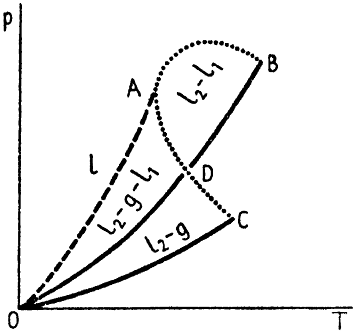


FIG. 41.

same way as the symbols a, b, c were used in § 61). The regions l and g contain the projections of liquid and gaseous states respectively, while the region g–l contains both liquid and gaseous states and also states in which phase separation occurs, and finally in the region gl above the critical line the distinction between gas and liquid disappears.

If in addition there is a line of equal concentrations, the projection on the p, T plane is as shown in Fig. 41. The line of equal concentrations may lie above OB or below OC but not between them. Of the various points shown only A, B, C are genuine intersections, D arising on account of the projection (i.e. actually, the critical line and the phase equilibrium curve corresponding to OB do not cross). The symbols l_1 and l_2 denote liquid phases with different concentrations. Above the line of equal concentrations only one liquid phase exists.

All these properties of the projections of the special lines on the p, T plane become self-evident if we examine the equilibrium diagram corresponding to the section of the equilibrium surface by planes of different constant temperatures for instance. Thus, the sections of the equilibrium surface by planes corresponding to temperatures less than that of A, and temperatures between A and B,

in Fig. 40, give equilibrium diagrams like those shown in Figs. 23 and 25, while a section by a plane corresponding to a temperature less than that of A on Fig. 41 gives an equilibrium diagram like Fig. 24.

If the two components have limited miscibility in the liquid phase, then a three-phase line exists. This line must necessarily terminate at some definite point (i.e. for definite values of p and T) since at

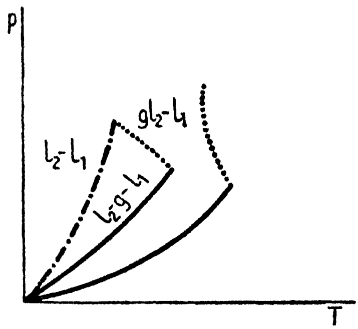


FIG. 42.

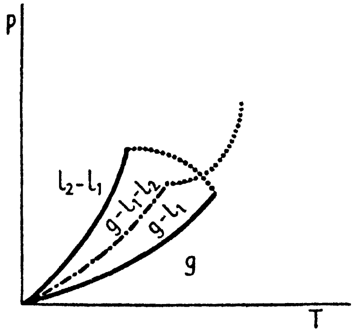


FIG. 43.

high temperatures there are no different phases, and at high pressures only liquid phases exist, so that a triple point is impossible in either case. The three-phase line can, however, terminate only at an intersection with some other special line. It cannot intersect the phase equilibrium curve of a pure component since this would mean that there was a triple point for the pure component, which is impossible, because in the present case the pure components can only have two phases (gas and liquid). Consequently the three-phase line must terminate at its intersection with the critical line.

Thus there are three end points of critical lines, at the ends of the phase equilibrium curves of the two pure components and at the end of the three-phase line, and correspondingly there must be two critical lines. These lines, however, cannot intersect (§ 63), and so one of them must continue either to the origin of coordinates or to infinity. Now at low temperatures every solution is dilute, and dilute solutions have no critical points (except those of the pure components); this follows from the fact that $(\partial\mu/\partial c)_{p,T}$ for dilute solutions is equal to kT/c (substituting the expression for the chemical potential of the solute) and so can nowhere be zero. Consequently the critical line cannot go to the origin of coordinates. Similarly, it cannot go off

in the direction of high temperatures since at high temperatures there is no distinction between phases. Thus the critical line must continue in the direction of high pressures. According as the projection of the three-phase line passes above or between the phase equilibrium curves of the two pure components, the projection diagram is of the type of Fig. 42 or of Fig. 43. The three-phase line cannot pass below these curves, i.e. in the region of gaseous states, since in the gaseous phase the two components can mix in arbitrary proportions.

X

CHEMICAL REACTIONS

65. Conditions for chemical equilibrium

In this chapter we shall discuss chemical reactions, i.e. processes in which the numbers of particles of the various species may change, and in which new species of particles may appear which were not present in the system before the process. In these processes the individual particles (atoms, ions, or molecules) may combine, forming new kinds of particles, or decompose into others. As is well known, chemical reactions can be described by means of symbolic equations, and if all the terms are collected on one side, these have the form

$$\sum_i \nu_i A_i = 0, \tag{65.1}$$

where A_i is the chemical symbol of the ith species taking part in the reaction and the ν_i are positive or negative integers (for instance in the reaction $O_2+2H_2 = 2H_2O$, or $O_2+2H_2-2H_2O = 0$, the coefficients are $\nu_{O_2} = 1$, $\nu_{H_2} = 2$, $\nu_{H_2O} = -2$).

A chemical reaction in a given system will continue until an equilibrium state (chemical equilibrium) is reached, for which the numbers of the various kinds of particle taking part in the reaction no longer change.

All chemical reactions generally take place in both directions, so that the process of combination of several particles into more complex particles, for instance, is accompanied by the reverse process of decomposition of the complex particles into simpler ones. Before equilibrium sets in, the process takes place more in one direction than the other, but once equilibrium has been established the two opposite processes take place to such an extent that the total numbers of each kind of molecule remain constant.

In this book we shall not concern ourselves with the actual course of the reaction, since this belongs to the sphere of kinetics (§ 4), but will limit ourselves to a discussion of chemical equilibrium, and first of all we have to deduce the conditions for this equilibrium, i.e. the relations between pressure, temperature, and the various concentrations in the equilibrium state.

Now it is evident that the equilibrium conditions are independent of the particular conditions of the reaction before equilibrium was

reached (i.e. whether the reaction took place at constant pressure and temperature, or at constant volume and temperature, etc.), and consequently in deducing the equilibrium conditions we are free to make any assumptions we wish about how the reaction took place. Suppose for instance that it took place at constant pressure and temperature. We know from § 17 that for such processes the Gibbs free energy of the system tends to a minimum, which it reaches in equilibrium, so when equilibrium has been established, $dG = 0$. Since the pressure and temperature are constant, i.e. $dp = 0$ and $dT = 0$, we have

$$dG = \sum_i (\partial G/\partial N_i)\, dN_i = 0,$$

where N_1, N_2,... are the numbers of particles of the various species taking part in the reaction, and since $\partial G/\partial N_i = \mu_i$ (the chemical potential of the ith species), this becomes

$$\sum \mu_i dN_i = 0. \tag{65.2}$$

It is easy to see that each of the dN_i must be proportional to the corresponding coefficient ν_i in (65.1). In fact, quite independently of how the reaction actually takes place, it can be considered formally as made up of 'elementary' reactions taking place between the numbers of particles indicated by the reaction equation. In such an 'elementary' reaction the number of particles of the ith species changes by ν_i, and so if dn such 'elementary' reactions have taken place the change of the number of particles of the ith species will be

$$dN_i = -\nu_i dn.$$

Substituting this in (65.2) we obtain

$$\sum \mu_i \nu_i = 0. \tag{65.3}$$

Thus *the condition of chemical equilibrium* is obtained by replacing the chemical symbols in the reaction equation by the corresponding chemical potentials. If several different chemical reactions are possible in the system, then the equilibrium condition is a system of equations similar to (65.3), each of the equations being obtained from the appropriate chemical reaction equation, in the way explained above.

66. The law of mass action

We shall now make concrete assumptions about the actual nature of the reacting substances, and first of all we shall discuss reactions taking place in a mixture of gases (assumed perfect).

We have for the chemical potential of the ith gas in the mixture (from (30.5))

$$\mu_i = kT \log p_i + \chi_i(T), \tag{66.1}$$

where p_i is the partial pressure of the ith gas. If c_i is the concentration of this gas (defined here as the ratio N_i/N, where N_i is the number of molecules of the ith gas and $N = \sum N_i$), and p the pressure of the whole mixture, then obviously $p_i = c_i p$. Substituting (66.1) into (65.3) we find as the condition for chemical equilibrium in a gaseous mixture:

$$\sum_i \nu_i \mu_i = kT \sum_i \nu_i \log p_{0i} + \sum_i \nu_i \chi_i = 0$$

(p_{0i} being the partial pressure in the state of chemical equilibrium), or

$$\sum_i \nu_i \log p_{0i} = -\frac{1}{kT} \sum_i \nu_i \chi_i.$$

Hence

$$\prod_i p_{0i}^{\nu_i} = e^{-\sum_i \nu_i \chi_i / kT},$$

or

$$\prod_i p_{0i}^{\nu_i} = A(T), \tag{66.2}$$

where $A(T)$ denotes $\exp[-\sum_i \nu_i \chi_i/kT]$.

If instead of p_{0i} we substitute pc_{0i}, where c_{0i} is the concentration in chemical equilibrium, (66.3) becomes

$$\prod_i c_{0i}^{\nu_i} = p^{-\sum_i \nu_i} A(T). \tag{66.3}$$

The expression on the right-hand side is usually called *the chemical equilibrium constant*, or, more briefly, the equilibrium constant; the form of its dependence on temperature cannot be deduced without further assumptions about the properties of the gases. The value of the equilibrium constant is independent of the initial quantities of the reacting gases.

The result that in the equilibrium state the product $\prod_i c_{0i}^{\nu_i}$ is a constant (for given p and T) is called *the law of mass action*.

An equation analogous to (66.3) can also be obtained for reactions in which all the components are in solution (we shall assume that the solution is dilute). The chemical potential of each of the solutes may be obtained from the Gibbs free energy (53.4) of a solution of several substances. Thus retaining only the first-order terms and differentiating with respect to the appropriate number of particles we obtain

$$\mu_i = kT \log c_i + \psi_i(p, T). \tag{66.4}$$

The concentration c_i is here the ratio of number of particles of the

ith solute to the number of particles of the solvent (since the solution is dilute, this definition is practically the same as that of the c_{0i} in (66.3)). Substituting (66.4) into (65.3) we obtain

$$kT \sum_i \nu_i \log c_{0i} = -\sum_i \nu_i \psi_i(p, T),$$

or

$$\prod_i c_{0i}^{\nu_i} = e^{-\sum_i \nu_i \psi_i / kT},$$

and introducing a function $K(p, T)$, equal to $e^{-\sum_i \nu_i \psi_i / kT}$, we have

$$\prod_i c_{0i}^{\nu_i} = K(p, T). \tag{66.5}$$

Thus the law of mass action applies also to reactions in dilute solutions. In contrast to the case of perfect gases, however, the dependence of the chemical equilibrium constant $K(p, T)$ on pressure is not specified.

If besides gases and substances in solution there are other substances taking part in the reaction, which are in a pure phase (i.e. not mixed with other substances in this phase), for instance pure solids, then the equilibrium condition gives an equation of the same form as (66.3) or (66.5). Since, however, the chemical potential in a pure phase depends only on pressure and temperature, the quantities of these additional pure reagents do not appear on the left-hand side, i.e. the product of the concentrations of the gases (or of the solutes) must be written as if these additional substances were not there. Their actual presence only affects the form of the pressure- and temperature-dependence of the chemical equilibrium constant.

If only gases and for instance solids take part in the reaction, the chemical potential of the solids can be assumed independent of pressure, since the pressures are generally comparatively small, and consequently the pressure-dependence of the equilibrium constant will still be that given by (66.3) (the index $\sum_i \nu_i$ on the right-hand side will refer, of course, only to the gaseous components).

EXAMPLE

Determine the equilibrium constant $A(T)$ for a gaseous reaction, under the assumption that the gases obey the equipartition law.

SOLUTION. Comparing (28.8) with (33.6) we find

$$\chi_i(T) = u_{0i} - c_{pi} T \log T + \beta T.$$

Hence, by the definition of $A(T)$, (66.2), we have,

$$A(T) = \text{const.}\, T^{\sum \nu_i c_{pi}/k} e^{-\sum \nu_i u_{0i}/kT}.$$

67. The heat of reaction

Chemical reactions are in general accompanied by the evolution or absorption of heat (*exothermic* and *endothermic* reactions respectively), and the quantity of heat depends, of course, on the conditions under which the reaction takes place. If the reaction takes place exothermally in one direction, it will be endothermic in the reverse direction.

As in the determination of the heat of solution (§ 58) we must first of all calculate the work which must be done to carry out the reaction, and we shall calculate the minimum possible work, which as we know, is that required when the reaction takes place reversibly. The same work is evidently the maximum work which can be obtained from the reverse process.

Thus we shall calculate the minimum work which has to be done to carry out some small number, δn, of 'elementary reactions'. We shall assume that the reaction takes place at constant pressure and temperature, so that the minimum work δW is equal to the change of Gibbs free energy. Since p and T are constant,

$$\delta W = \delta G = \sum_i (\partial G/\partial N_i)\,\delta N_i,$$

where the summation is over all the species of substances reacting, and δN_i is the change in number of the molecules of the ith species for δn 'elementary reactions'. As already explained (§ 65), we have

$$\delta N_i = -\nu_i\,\delta n,$$

where ν_i is the coefficient of the corresponding chemical symbol in the reaction equation. Also we have $\partial G/\partial N_i = \mu_i$, so we obtain

$$\delta W = -\delta n \sum_i \mu_i \nu_i, \tag{67.1}$$

and $\sum_i \mu_i \nu_i$ is consequently the work per 'elementary reaction'. As we should expect, this work vanishes in chemical equilibrium, since then $\sum \mu_i \nu_i = 0$.

If the reaction takes place between perfect gases, then using (66.1) for μ_i we find

$$\delta W = -\delta n(kT \sum_i \nu_i \log p_i + \sum_i \nu_i \chi_i),$$

or introducing, as in the previous section, $A(T) = e^{-\Sigma \nu_i \chi_i/kT}$

$$\delta W = -\delta n\, kT\{\sum \nu_i \log p_i - \log A(t)\}. \tag{67.2}$$

For a reaction in solution we find analogously, using (66.4) for μ_i,

$$\delta W = -\delta n(kT \sum \nu_i \log c_i + \sum \nu_i \psi_i),$$

or, as in § 66, introducing $K(p, T) = e^{-\Sigma \nu_i \psi_i / kT}$ (the chemical equilibrium constant),

$$\delta W = -\delta n\, kT\{\sum \nu_i \log c_i - \log K(p, T)\}. \qquad (67.3)$$

We can now determine the quantity of heat absorbed (or evolved, according to the sign obtained) for δn elementary reactions. By equation (17.19) this heat δQ_p for the reaction at constant pressure and temperature is

$$\delta Q_p = -T^2 \frac{\partial}{\partial T}\left(\frac{W}{T}\right)_p.$$

In particular, for a gaseous reaction (substituting (67.2))

$$\delta Q_p = -kT^2 \delta n\, \partial \log A(T)/\partial T \qquad (67.4)$$

and for a reaction in solution (from (67.3))

$$\delta Q_p = -kT^2 \delta n\, \partial \log K(p, T)/\partial T. \qquad (67.5)$$

It is important to notice that δQ_p is directly proportional to δn and does not depend on the concentration at the given moment, so that these formulae apply for any value of δn.

We shall now determine the change of volume in a reaction taking place at constant pressure. It was shown in § 58 that this change is equal to the derivative with respect to pressure of the minimum work necessary to carry out the given process (see (58.5)). Hence the change of volume δV at constant pressure and temperature, for δn elementary reactions, is

$$\delta V = \partial(\delta W)/\partial p.$$

In particular, for reactions in solution we obtain (substituting (67.3))

$$\delta V = \delta n\, kT\, \partial \log K(p, T)/\partial p. \qquad (67.6)$$

In the case of gaseous reactions there is no need for a special formula for the change of volume, since the volume of a perfect gas at given p and T follows immediately from the number of particles and Clapeyron's equation.

In conclusion we may point out that equations (67.4–6) are in agreement with the Le Chatelier-Braun principle. Suppose for ininstance that the reaction is endothermic in one direction, then if the system in chemical equilibrium is warmed, the reaction will begin in this direction, so as to absorb heat in order to oppose the influence taking the system out of equilibrium. The same follows from (67.4) or (67.5); in this case δQ is positive and so the chemical equilibrium

constant diminishes with rise of temperature, i.e. the reaction will go further.

Similarly, if the volume is diminished by the reaction (at constant pressure), the Le Chatelier-Braun principle shows that an increase of pressure applied to the system in equilibrium will make the reaction go in such a direction as to decrease the volume, and so tend to compensate the increase of pressure. The same follows also from (67.6).

XI

ANISOTROPIC BODIES

68. Anisotropic bodies

BODIES may be either *isotropic* or *anisotropic*, according as the properties of the bodies are the same, or not the same, in all directions, and there are two kinds of anisotropic bodies: *solid crystals* and *liquid crystals*. There is no difference in principle between gases, liquids, and amorphous solids; they differ only in the degree of interaction of their molecules. The property of anisotropy possessed by crystals, however, distinguishes them fundamentally from liquids or amorphous solids.

It is easily shown that all positions in space of a particle in an isotropic body are equally probable; for if some positions were more probable than others, the properties of the body would not be the same in all directions (for instance they would not be the same along the direction of the line joining two maxima of probability and some other direction).

In solid crystals, on the other hand, the probabilities of finding atoms at various places in the crystal are different and usually have sharp maxima, corresponding to the fact that the atoms execute only quite small oscillations about equilibrium positions (called *lattice points*) which coincide with these maxima. Thus solid crystals are always solids in the sense of § 34. Since the arrangement of the lattice points in a crystal corresponds to an equilibrium state, it is a special arrangement, i.e. one selected from all the possible arrangements, and consequently is regular; the lattice points together make up the crystalline lattice.

It is the regularity of the arrangement of the lattice which distinguishes solid crystals from solid amorphous bodies; for though in the latter the atoms also carry out only small vibrations, their mean positions are distributed in a disordered way. In fact, these mean positions in the amorphous solid do not correspond to any equilibrium; in the course of time they move about, and on the average all positions of atoms are equally probable.

Every crystalline lattice has certain definite symmetry properties, which are determined by the transposals (displacements, rotations, reflections) or *the transformations*, as they are called, *which bring the*

lattice into coincidence with itself; each such transformation is also called a symmetry element, and lattice points which are brought into coincidence by the transformation are said to be equivalent.

As we have already pointed out, if all positions of atoms in a body are not equally probable, the body is necessarily anisotropic; the converse is not, however, true, for even if all positions are equally probable, the body may still be anisotropic: this is so in the case of liquid crystals. Thus if the molecules have some preferential axis (e.g. if they are of elongated shape), the axes of all the molecules may point the same way and even though all positions of the molecules (i.e. of their centres of gravity) are equally probable, the body will evidently be anisotropic. The structure of a liquid crystal can be described in a more general way by saying that although every position of an atom in a liquid crystal is equally probable, once the position of one atom is given the various possible positions for neighbouring atoms are no longer equally probable.

At absolute zero all atoms are at rest, and since the potential energy must be a minimum, the atoms must be arranged regularly. Thus *all bodies should be crystalline at absolute zero.*† This refers, however, only to bodies in equilibrium; if the body is not in equilibrium (e.g. a supercooled liquid) it need not be crystalline at absolute zero.

If the number of lattice points which can be occupied by atoms of a given species is equal to the number of these atoms available, then there will be an atom close to each lattice point, or in other words the probability of finding an atom close to a lattice point will always be unity. In this case the crystal is said to be *completely ordered*. Suppose now that some of the atoms can leave their correct places (i.e. the places they would occupy in the fully ordered crystal) to occupy some other places, so that new lattice points appear. In this case the number of lattice points becomes greater than the number of available atoms, and obviously the probability of finding an atom close to a lattice point is less than one. The crystal is now said to be *incompletely ordered.*

Often the old and the new lattice points are completely similar geometrically, and differ only in the probability of occupation by atoms of the given species. In this case the probability of occupation

† Helium, which can still remain liquid at absolute zero, is, however, an exception. This is connected with deviations from classical mechanics, i.e. it is due to quantum effects.

of an old lattice point is always higher than that of a new one (this is merely a matter of convention, for if it were lower we should call the new lattice points old, and vice versa). If now the probabilities of occupation of the new and of the old lattice points become equal (not equal to unity, of course), then evidently all the lattice points become equivalent, and the symmetry of the lattice is increased (i.e. new symmetry elements appear). The crystal is then

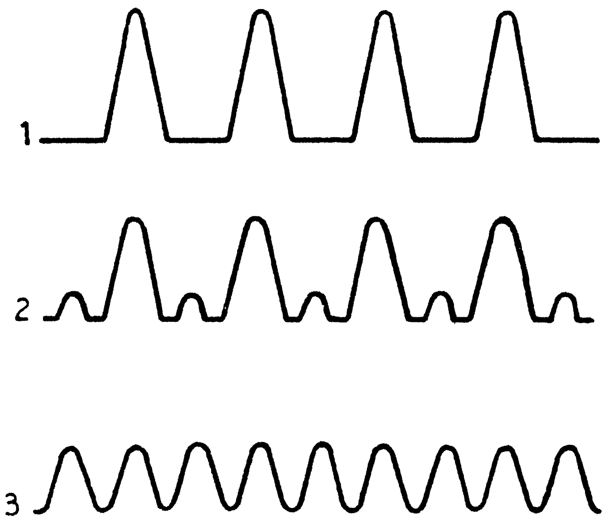


FIG. 44.

said to be *disordered*. In general, disorder is always associated with lattice points becoming equivalent, which were not equivalent (in the completely or incompletely ordered crystal). In future we shall refer to completely and incompletely ordered crystals simply as ordered, since they both possess the same symmetry, in contrast to disordered crystals which have a different symmetry. It should be noticed that sometimes a crystal may be ordered in one respect, and yet be disordered in another.

We shall now illustrate these considerations by an example. Suppose the probability distribution in the lattice has the form of the curves in Fig. 44 (we show this distribution in one-dimensional form, but this is of course only schematic). If the distribution is represented by curve 1, where the probability of finding an atom near each maximum (i.e. the area of each 'tooth') is unity, then the crystal is fully ordered. If, however, auxiliary maxima appear

between the 'teeth' so that the probabilities are not unity near either kind of maximum (curve 2), the crystal is incompletely ordered. Finally, if all the maxima become equal (to a half, of course) the crystal will be disordered (curve 3). In the last case the number of atoms occupying the places they would occupy in the fully ordered

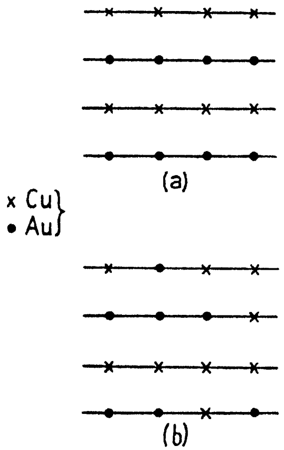


FIG. 45.

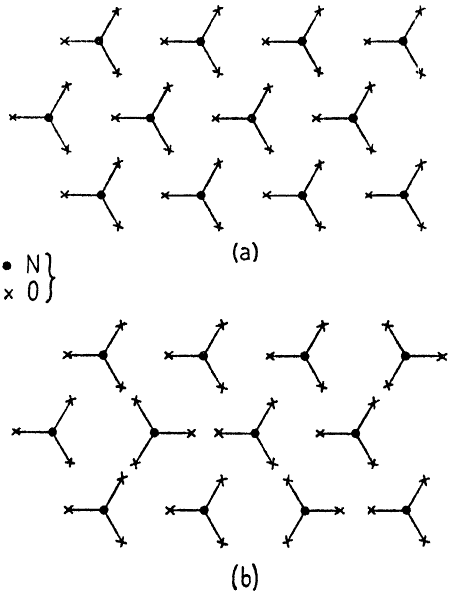


FIG. 46.

crystal is equal to the number occupying new places. It is easy to see that this increases the symmetry of the lattice, and that a new periodicity appears with a period equal to half that of the initial one.

From what was said above about the arrangement of atoms at absolute zero it follows that crystals are fully ordered at absolute zero (if, of course, the crystal is in equilibrium); reduction of the degree of order can take place only at high temperatures.†

† For further illustration we give two concrete examples of ordered and disordered crystals.

(1) In the fully ordered crystal of the alloy CuAu, the Cu and Au atoms occupy lattice points lying in alternate parallel planes (Fig. 45 *a*). The lattice points in any layer are equivalent to those in the next but one; the crystal has tetragonal symmetry. If some of the Cu atoms go into layers which should be occupied by Au atoms, and vice versa, the crystal becomes incompletely ordered (Fig. 45 *b*). In other words there is a certain probability of finding Cu and Au atoms in 'wrong' places. Eventually if the number of Cu and Au atoms in 'wrong' places becomes equal to those in their 'correct' places the crystal is disordered; all the lattice points are then

69. Transition points

When the state of a body changes, its symmetry properties may also change, but they cannot change gradually; a change of symmetry can in fact only take place abruptly, since a symmetry element has to be either present or absent. Consequently *the transition of a body from a state of one symmetry to a state of different symmetry cannot take place continuously.* In particular it is impossible to have a continuous transition from an anisotropic body to an isotropic one (for instance from a crystal to a liquid).

There are two possible kinds of transition associated with a change of symmetry of a body. In the first of these the probability distribution in the lattice changes abruptly together with the sudden change from one symmetry to another (the usual case is a change of the positions of the lattice points). Transitions of this kind are those between two phases of different symmetries, and at the actual transition point (which we shall call the *phase transition point*) we have two bodies in different states, in equilibrium with each other. In a phase transition between two states of different symmetries the change of symmetry may sometimes be connected with a transition from an ordered to a disordered state (or the reverse), but in general it is not usually connected with a change of order (the more usual case is a transition between ordered crystals of different symmetries).

A particular case of a phase transition is that between an anisotropic and an isotropic phase (transitions between crystal and liquid or gas). We may point out that only two phases (liquid and gas) are possible for isotropic bodies, but a variety of phases (called *modifications*) are possible for anisotropic bodies (i.e. crystals with a variety of symmetries).

The other kind of transition is one in which although a number of symmetry elements appear or disappear abruptly, the probability

equivalent, the period of the lattice is halved, i.e. the symmetry is increased, and moreover the crystal assumes cubic symmetry.

(2) The crystal $NaNO_3$ consists of alternate layers of Na atoms and NO_3 groups. In the latter the N atoms are arranged at the corners of equilateral triangles and the O atoms in triangles round the N atoms. The NO_3 groups may, however, be orientated in either of two directions; in the fully ordered crystal they all point the same way (Fig. 46 *a*), and the crystal has an axis of trigonal symmetry. If some of the NO_3 groups become orientated the opposite way, the crystal is incompletely ordered, and finally if the numbers of NO_3 groups orientated in the two opposite ways become equal, the crystal is disordered. The probabilities of the two orientations for an NO_3 group are then equal, and the crystal symmetry becomes hexagonal instead of trigonal.

distribution in the lattice differs only very slightly before and after the transition; for further change of state, however, the probability distribution deviates more and more from its initial form. We shall call this kind of transition point a *Curie point*; it is sometimes called a 'phase transition point of the second kind', or a 'λ-point'. It is important to remember that the symmetry can change abruptly even for an infinitesimal change of the probability distribution (this is illustrated more fully below). Thus we can say that in passing a Curie point the symmetry always changes abruptly, and the probability distribution (i.e. the state of the body) continuously, while in passing a phase transition point both change abruptly. Moreover, at the Curie point itself, the states corresponding to the two symmetries coincide, while at a phase transition point two different phases of the body coexist in equilibrium.

These considerations can be illustrated by the same example as in § 68. Thus suppose the probability distribution of the atoms in the lattice is represented by curve 2 in Fig. 44, then if the smaller maxima increase, the lattice continues to have the same symmetry, until all the maxima become equal. At the moment when they become equal (curve 3), the lattice suddenly acquires the new symmetry (which is easily seen to be a higher symmetry than the initial one), but there is no abrupt change in the probability distribution.

A Curie point usually occurs for transitions between ordered and disordered states. With increase of temperature the probability distribution in the lattice of an ordered crystal changes, until at the Curie point the crystal becomes disordered. It should be emphasized that it is the higher temperature which corresponds to the disordered state (of higher symmetry) and the lower to the ordered state (of lower symmetry).

It is convenient to describe the transition through a Curie point by means of a variable η, which determines the deviation of the probability distribution of an ordered crystal (i.e. of lower symmetry) from that of the disordered crystal (i.e. with higher symmetry). This variable is defined in such a way that it vanishes for the disordered state, and has non-zero positive or negative values for ordered states.

The Gibbs free energy G can be expressed as a function of p, T and η; on one side of the Curie point (in the disordered state), $\eta = 0$, so that for this state to be stable, G as a function of η must have a

minimum at $\eta = 0$. Expanding $G(p, T, \eta)$ in powers of η near the Curie point (η is close to zero near the Curie point) we obtain

$$G(p, T, \eta) = G_0 + G_1\eta + G_2\eta^2 + G_3\eta^3 + G_4\eta^4 + \dots \qquad (69.1)$$

(the quantities G_0, G_1, etc., are functions of p and T). In the disordered state $G = G_0$, and in order that this should correspond to a minimum of G it is necessary that

$$(\partial G/\partial\eta)_{\eta=0} = 0 \quad \text{and} \quad (\partial^2 G/\partial\eta^2)_{\eta=0} > 0.$$

This means that $G_1(p, T) = 0$ everywhere on the disordered side of the Curie point, and so $G_1(p, T)$ has to vanish identically (this is possible if, and only if, the states with $\eta = 0$ and $\eta \neq 0$ differ in their symmetry), and also $G_2(p, T) > 0$ for the disordered state.

In the ordered states we must have $G_2 < 0$, so that the minimum of G should correspond to values of η different from zero. Consequently at the actual Curie point G_2 must vanish:

$$G_{2c}(p, T) = 0. \qquad (69.2)$$

But in order that the Curie point itself should be a stable state, i.e. in order that G as a function of η should be a minimum there too, we must have G_3 zero and G_4 positive at the Curie point:

$$G_{3c}(p, T) = 0, \qquad G_{4c}(p, T) > 0. \qquad (69.3)$$

There are two possible cases. The function $G_3(p, T)$ may be everywhere identically zero on account of a particular symmetry of the body, and then only the condition $G_{2c}(p, T) = 0$ is left to determine the Curie point so that we have a *line of Curie points*, determined by the implicit equation $G_{2c}(p, T) = 0$, between p and T. If, however, G_3 is not identically zero, then the Curie point is determined by the two equations $G_{2c} = 0$ and $G_{3c} = 0$, and the Curie points must be isolated points.

The most interesting case, of course, is when there is a line of Curie points; this is the case which usually occurs in practice, and we shall now examine it further, i.e. in future we shall assume that $G_3 \equiv 0$. It will be noticed that this is always the case if states differing only in the sign of η are identical. For instance in the example of § 68 (Fig. 44) we can choose η to be the difference between the number of atoms in the places they would occupy for the completely ordered state (i.e. the lattice points of curve 1) and the number of atoms in the new lattice points. Then evidently for the disordered state (curve 3) $\eta = 0$. A change of sign of η in this example means only

an exchange of all the lattice points of one type for the lattice points of the other type, which evidently leads to an identical state. In particular, the states $\pm\eta$ are identical, if the number of lattice points which can be occupied by atoms of a given species is double the number of available atoms of this species.

Thus for the case of a line of Curie points we may describe the state of order by the essentially positive variable $\xi = \eta^2$. The variation of ξ in passing the Curie point is then represented by a curve like that in Fig. 47 (C being the Curie point), showing how ξ varies with T for some given value of p. Near the Curie point the expansion of G (69.1) now becomes

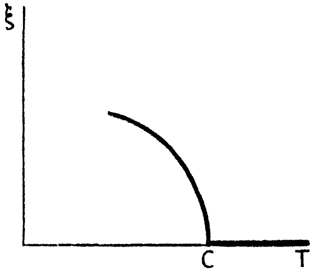


FIG. 47.

$$G(\xi, p, T) = G_0(p, T) + \alpha(p, T)\xi + \tfrac{1}{2}\beta(p, T)\xi^2. \tag{69.4}$$

The quantity α (which corresponds to G_2) vanishes, and the quantity β (corresponding to G_4) is positive, at the Curie point, i.e.

$$\alpha_c(p, T) = 0, \qquad \beta > 0. \tag{69.5}$$

The dependence of ξ on p and T near the Curie point is determined by the condition that in the ordered state, G as a function of ξ must have a minimum, i.e. $\partial G/\partial\xi = 0$, hence

$$\xi = -\alpha/\beta. \tag{69.6}$$

It should be remembered that $\alpha < 0$ in the ordered state and $\alpha > 0$ in the disordered state (corresponding to what was said about G_2 above).

We shall now find the entropy close to the Curie point. From (69.4) we find immediately (neglecting higher order terms),

$$S = -\partial G/\partial T = S_0 - \xi\,\partial\alpha/\partial T, \tag{69.7}$$

where S_0 is the entropy in the disordered state. At the actual Curie point $\xi = 0$ and therefore $S = S_0$, so we see that the entropy is continuous through the Curie point, and *no heat is emitted or absorbed in a Curie point transition.* Similarly, it is easy to show that the energy and the volume of the body are also continuous through the Curie point.

Substituting (69.6) into (69.7), the entropy of the ordered state becomes

$$S = S_0 + \frac{\alpha}{\beta}\frac{\partial\alpha}{\partial T}. \tag{69.8}$$

Hence we can find the specific heat C_p in the ordered state:

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = C_{p0}+\frac{T}{\beta}\left(\frac{\partial \alpha}{\partial T}\right)^2-\frac{\alpha}{\beta^2}\frac{\partial \alpha}{\partial T}\frac{\partial \beta}{\partial T},$$

where C_{p0} is the specific heat of the disordered state.

At the Curie point itself we have $\alpha = 0$ (by (69.5)), so

$$C_p^c = C_{p0}^c+\frac{T}{\beta^2}\left(\frac{\partial \alpha}{\partial T}\right)^2. \tag{69.9}$$

Thus there is a jump in specific heat at the Curie point, equal to $T(\partial\alpha/\partial T)^2/\beta$, and since $\beta > 0$ we see that the *specific heat increases in the transition from the disordered to an ordered state*, i.e. from the more to a less symmetrical state.

We shall now determine by thermodynamic reasoning the relations between the discontinuities of certain thermodynamic quantities at the Curie point. We have seen that the volume and entropy are continuous at the Curie point, i.e. their discontinuities ΔS and ΔV are zero:

$$\Delta S = 0, \qquad \Delta V = 0. \tag{69.10}$$

Differentiating these equations with respect to temperature along the Curie point curve, i.e. considering p as a function of T, we obtain

$$\left.\begin{aligned} &\Delta\left(\frac{\partial V}{\partial T}\right)_p+\frac{dp}{dT}\Delta\left(\frac{\partial V}{\partial p}\right)_T = 0 \\ \text{and}\qquad &\frac{\Delta C_p}{T}-\frac{dp}{dT}\Delta\left(\frac{\partial V}{\partial T}\right)_p = 0 \end{aligned}\right\} \tag{69.11}$$

(since $(\partial S/\partial p)_T = -(\partial V/\partial T)_p$). These two equations connect the jumps of specific heat C_p, of the coefficient of thermal expansion $(\partial V/\partial T)_p$, and of the coefficient of compressibility $(\partial V/\partial p)_T$ at the Curie point.

Similarly, differentiating the equations $\Delta S = 0$ and $\Delta p = 0$ (the pressure is, of course, also continuous) along the Curie point curve, but using V and T as variables, we find

$$\left.\begin{aligned} &\Delta\left(\frac{\partial p}{\partial T}\right)_V+\frac{dV}{dT}\Delta\left(\frac{\partial p}{\partial V}\right)_T = 0 \\ \text{and}\qquad &\frac{\Delta C_v}{T}+\frac{dV}{dT}\Delta\left(\frac{\partial p}{\partial T}\right)_V = 0. \end{aligned}\right\} \tag{69.12}$$

From (69.11) and (69.12) we obtain the jumps in C_p, C_v, $(\partial p/\partial T)_V$, and $(\partial V/\partial T)_p$ in terms of the jump in $(\partial V/\partial p)_T$:

$$\left.\begin{aligned}\Delta\left(\frac{\partial V}{\partial T}\right)_p &= -\frac{dp}{dT}\Delta\left(\frac{\partial V}{\partial p}\right)_T, & \Delta C_v &= T\left(\frac{dV}{dT}\right)^2\Delta\left[1\Big/\left(\frac{\partial V}{\partial p}\right)_T\right],\\ \Delta\left(\frac{\partial p}{\partial T}\right)_V &= -\frac{dV}{dT}\Delta\left[1\Big/\left(\frac{\partial V}{\partial p}\right)_T\right], & \Delta C_p &= -T\left(\frac{dp}{dT}\right)^2\Delta\left(\frac{\partial V}{\partial p}\right)_T.\end{aligned}\right\} \quad (69.13)$$

70. The critical Curie point

Transition curves (in the p, T diagram, for instance) between phases of different symmetries (either phase equilibrium curves or lines of Curie points) cannot terminate in the same way as a gas-

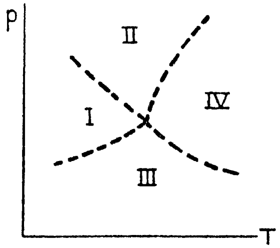


FIG. 48.

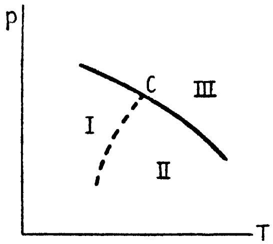


FIG. 49.

liquid equilibrium curve, for if they did it would be possible to construct a continuous transition path (above the terminal point) between states corresponding to different symmetries.

Consequently the transition curve between two phases of different symmetries can terminate only by meeting another such transition curve; we shall now consider the various possible types of intersection. The intersections of phase equilibrium curves have already been dealt with; the intersection of lines of Curie points is shown in Fig. 48. One of the regions, I, say, is the least symmetrical phase, states in II possess some other symmetry elements in addition to those of I, and those in III possess some different additional symmetry elements, while those in IV possess all these symmetry elements, and so correspond to the highest symmetry.

If the line of Curie points intersects a phase equilibrium curve, one of the lines must terminate at the intersection (Figs. 49, 50). At the point C phases I and II become identical in the case of Fig. 49, and phases I, II, and III become identical in the case of Fig. 50.

Finally, the phase equilibrium curve and the line of Curie points may pass into each other at some point K (Fig. 51), and we shall show below that the two curves meet continuously in this case. We

shall call a point of this type a *critical Curie point*, and we shall investigate its properties in this section.

We saw in § 69 that in the expansion of the Gibbs free energy G in powers of η,

$$G = G_0+G_1\eta+G_2\eta^2+G_3\eta^3+G_4\eta^4+G_5\eta^5+G_6\eta^6+... \quad (70.1)$$

the coefficient G_1 is always zero, and if there is a Curie point line (as in the present case), then G_3 is also identically zero. Moreover, on

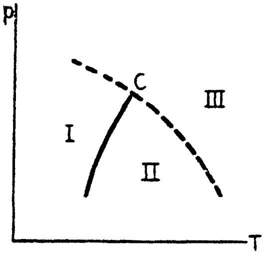


Fig. 50.

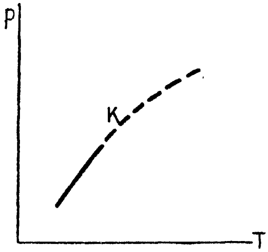


Fig. 51.

the Curie line itself G_2 vanishes and G_4 is positive, and evidently the converse is true that points for which these conditions hold are Curie points. Consequently in passing the point where the line of Curie points meets the phase equilibrium curve, i.e. in passing through the critical Curie point, G_4 changes sign, and so at the actual critical point

$$G_{2K} = 0, \qquad G_{4K} = 0. \quad (70.2)$$

But then in order that the critical Curie point should correspond to a stable state, i.e. in order that G as a function of η should have a minimum, we must have $G_{5K} = 0$ and $G_{6K} > 0$. This is possible only if G_{5K} has to be identically zero for reasons of symmetry, as otherwise we should have three equations with two unknowns (p and T) for the critical Curie point, and these have no solution in general. We may remark that $G_5 \equiv 0$ is true, anyhow, for those cases where states differing only in the sign of η are identical.

As in the preceding section, we may now replace η by $\xi = \eta^2$, and the expansion of $G(p, T, \xi)$ has the form

$$G(p,T,\xi) = G_0(p,T)+\alpha(p,T)\xi+\tfrac{1}{2}\beta(p,T)\xi^2+\tfrac{1}{3}\gamma(p,T)\xi^3, \quad (70.3)$$

where by the above considerations

$$\alpha_K = 0, \qquad \beta_K = 0, \qquad \gamma_K > 0. \quad (70.4)$$

In the ordered state ξ is determined as in § 69, by the condition that G has a minimum, i.e. $\partial G/\partial\xi = 0$ and $\partial^2 G/\partial\xi^2 > 0$, hence

$$\partial G/\partial\xi = \alpha+\beta\xi+\tfrac{1}{2}\gamma\xi^2 = 0, \qquad \partial^2 G/\partial\xi^2 = \beta+\gamma\xi > 0, \tag{70.5}$$

and we obtain ξ as a function of p,T in the form

$$\xi = [-\beta+(\beta^2-2\alpha\gamma)^{\frac{1}{2}}]/\gamma \tag{70.6}$$

(the plus sign is taken for the square root, in order to satisfy the second condition of (70.5)).

Knowing G we can calculate the entropy

$$S = -\partial G/\partial T = S_0-\xi\,\partial\alpha/\partial T$$

(neglecting higher powers of ξ). Substituting for ξ from (70.6) we obtain for the entropy of the ordered state

$$S = S_0+\frac{\beta}{\gamma}\frac{\partial\alpha}{\partial T}-\frac{1}{\gamma}\frac{\partial\alpha}{\partial T}(\beta^2-2\alpha\gamma)^{\frac{1}{2}}, \tag{70.7}$$

where S_0 as in § 69 is the entropy of the disordered state.

We can now determine the specific heat C_p near the critical Curie point. It will be seen that the temperature derivative of the last term in (70.7) becomes infinite at the critical Curie point, since it contains $\sqrt{(\beta^2-2\alpha\gamma)}$ in the denominator and α and β both vanish at the critical Curie point. Since the derivatives of the first two terms remain finite, they may be neglected in comparison with that of the third term. Thus for the specific heat of the ordered (i.e. less symmetrical) state near the critical Curie point we obtain the expression

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = T\left(\frac{\partial\alpha}{\partial T}\right)^2\Big/\sqrt{(\beta^2-2\alpha\gamma)} \tag{70.8}$$

(the other terms obtained in the differentiation of the third term of (70.7) have been omitted since they vanish at the critical Curie point together with α and β).

In (70.8) we can, without much loss of accuracy, substitute T_K the temperature of the critical Curie point for T in the numerator. We shall also introduce the temperature T_0 for which (at given pressure) $\beta^2-2\alpha\gamma = 0$. At the critical Curie point evidently $T_0 = T_K$, and close to the critical Curie point T_0 is close to T_K, so we can expand the expression under the square root in (70.8) in powers of $(T-T_0)$, retaining only the first-order term. This gives

$$\beta^2-2\alpha\gamma = -2\left(\gamma\frac{\partial\alpha}{\partial T}\right)_{T=T_0}(T-T_0) \tag{70.9}$$

(the terms proportional to α and β have again been omitted since α and β are small near the critical Curie point). Thus finally we obtain

$$C_p = \frac{A}{\sqrt{(T_0 - T)}}, \tag{70.10}$$

where

$$A = \sqrt{\left(\frac{T_K^2(\partial\alpha/\partial T)^3_{T=T_K}}{2\gamma_K}\right)}$$

(the value of the coefficient of $T - T_0$ in (70.9) may of course be taken at T_K instead of T_0). Thus *at the critical Curie point the specific heat of the ordered state becomes infinite as* $(T_0 - T)^{-\frac{1}{2}}$.

For states lying on the actual line of Curie points, near the critical Curie point, the specific heat of the ordered state may be obtained directly from (70.8), since $\alpha = 0$ for a Curie point, and we obtain

$$C_p^c = \frac{T_K}{\beta}\left(\frac{\partial\alpha}{\partial T}\right)^2 \tag{70.11}$$

(there is no great loss of accuracy in putting T_K for T in the numerator). At the critical Curie point β is zero, and close to it it is proportional to the distance from it; in particular it is proportional to the difference $p - p_K$ between the pressure at the given point on the Curie curve and the pressure at the critical Curie point.

Let us now find the specific heat of the ordered state on the phase equilibrium curve, again near the critical Curie point. At a phase transition point, the transition between the ordered and disordered states occurs discontinuously (§ 69), in other words the two phases are in equilibrium at this point. The equilibrium condition, as we have seen, is the equality of the chemical potentials of the two phases, or, what is equivalent, the equality of their Gibbs free energies. Thus ξ, the degree of order of the ordered phase at the transition point is determined by the condition

$$G(\xi) = G(0) \tag{70.12}$$

(since $\xi = 0$ in the disordered phase). Substituting (70.3) for G, we obtain

$$\alpha + \tfrac{1}{2}\beta\xi + \tfrac{1}{6}\gamma\xi^2 = 0.$$

Moreover, in the ordered phase the condition (70.5) must hold, i.e.

$$\partial G/\partial\xi = \alpha + \beta\xi + \tfrac{1}{2}\gamma\xi^2 = 0.$$

Eliminating γ from these two equations we obtain

$$\xi = -4\alpha/\beta, \tag{70.13}$$

and substituting this into one of the equations we have the condition

$$8\alpha\gamma = 3\beta^2. \tag{70.14}$$

This equation gives the relation between p and T along the phase equilibrium curve.

The specific heat of the ordered phase on the phase equilibrium curve near the critical Curie point is now obtained simply by substituting (70.14) into (70.8), which gives

$$C_p^{(\phi)} = \frac{2T_K}{|\beta|}\left(\frac{\partial\alpha}{\partial T}\right)^2. \tag{70.15}$$

Comparing with (70.11) we see that *the specific heat on the phase transition curve near the critical Curie point is twice as great as on the line of Curie points, for the same distance from the critical Curie point.*

We can also determine the heat of transition from the ordered to the disordered phase at transition points close to the critical Curie point. This heat is given by

$$Q = T_K(S-S_0) = T_K\frac{4\alpha}{\beta}\frac{\partial\alpha}{\partial T} = T_K\frac{3\beta}{2\gamma}\frac{\partial\alpha}{\partial T} \tag{70.16}$$

(we use (69.7) for S and (70.13) for ξ, and also make use of (70.14)). Multiplying Q by the specific heat $C_p^{(\phi)}$ of the ordered phase on the phase equilibrium curve (see (70.15)) we find

$$QC_p^{(\phi)} = T_K^2\frac{3}{\gamma}\left(\frac{\partial\alpha}{\partial T}\right)^3 = 6A^2,$$

where A is the coefficient in (70.10). Near the critical Curie point, β is proportional to $(p-p_K)$, as has been already mentioned, and so Q is also proportional to this difference.

In conclusion, we shall show that the phase equilibrium curve passes continuously (without a kink) into the line of Curie points, i.e. that dT/dp is continuous along the curves and has no jump at the critical Curie point. On the line of Curie points the p, T relation is determined by the condition $\alpha = 0$. Hence dT/dp is determined from the condition $d\alpha = 0$. On the phase equilibrium curve the p, T relation is determined by (70.14) and so dT/dp is determined by

$$4\gamma\, d\alpha + 4\alpha\, d\gamma - 3\beta\, d\beta = 0,$$

and at the critical Curie point (where $\alpha = \beta = 0$) this also becomes $d\alpha = 0$, i.e. coincides with the condition determining dT/dp on the line of Curie points. Consequently dT/dp has no discontinuity at the

critical Curie point; it can be shown, however, that there is a jump in $\partial^2 T/\partial p^2$ at this point.

At the critical Curie point C_p has an infinite jump, as we have seen, and it follows from (69.13) that $(\partial V/\partial p)_T$ and $(\partial V/\partial T)_p$ for the ordered phase become infinite at the critical Curie point. As regards C_v and $(\partial p/\partial T)_V$, they do not become infinite but have only a finite discontinuity, since $1/(\partial V/\partial p)_T$ has a finite discontinuity; this is in agreement with the considerations of § 36.

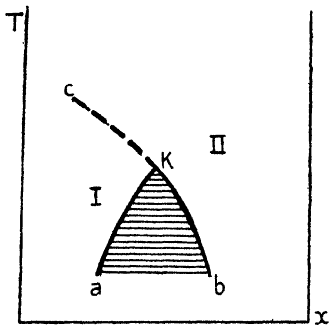


FIG. 52.

In conclusion we may mention the critical Curie points which can occur in the case of solutions. It can be shown that in the neighbourhood of such a point the equilibrium diagram has the appearance of Fig. 52 (the axes are temperature, T, and concentration, x). The curves Ka and Kb are phase equilibrium curves and Kc is a line of Curie points. The shaded area aKb is the region of phase separation into two phases, I and II, phase I being the less symmetrical (ordered) and phase II the more symmetrical (disordered). K is the critical Curie point; aK meets cK at an angle, and bK passes continuously into Kc. It can be shown also that in the case of solutions, the specific heat C_p has only a finite discontinuity at the critical Curie point.

71. Isolated Curie points

We saw in § 69 that if the coefficient $G_3(p, T)$ in the expansion of G in powers of η is not identically zero, only isolated Curie points are possible. This will occur, in particular, if the number of lattice points which can be occupied by atoms of a given species is three times as great as the number of these atoms available; in other words, if there are three types of lattice points which can be occupied by these atoms. Deviations from order then occur if besides atoms in lattice points of type 1 some atoms occupy lattice points of types 2 and 3 (it can be shown that the number of occupied lattice points of types 2 and 3 will be equal in this case). In the disordered crystal the numbers of atoms occupying all three types of lattice points will be equal; we can therefore define the 'degree of order' η as the difference between the numbers of atoms in lattice points of type 1

and those in lattice points of type 2 (or type 3). Evidently in this case states differing in the sign of η are physically different, since for one sign the lattice points of type 1 will contain more atoms than types 2 or 3, while for the opposite sign, the majority will be equally distributed among the two types 2 and 3.

It can be shown that in the neighbourhood of an isolated Curie point the p, T diagram has the form shown in Fig. 53; the Curie point C lies at the intersection of two phase equilibrium curves one of which terminates there. Above the curve aCb is the region corresponding to the disordered (more symmetrical) phase; the curve cC separates the regions corresponding to the two ordered phases I and II. These two phases can be shown to have the same symmetry and differ only in the sign of the degree of order η. At the point C all three phases become identical.

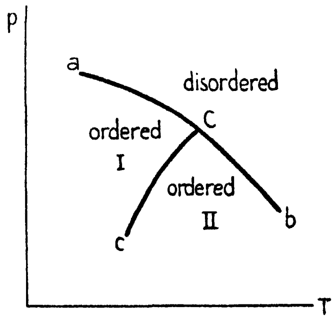


Fig. 53.

Moreover, it can be shown that *it is impossible to have a line of Curie points for a transition between a liquid and solid crystal, only isolated Curie points being possible.* We may note that as yet no case of an isolated Curie point has been experimentally observed. In conclusion we may also remark that in some cases it is necessary to introduce more than one variable η to specify the degree of order, but it can be shown that this does not affect any of the results we have obtained.

72. Ordered solid solutions

In this section we shall discuss a solid crystal containing two different substances, i.e. a solid solution. If the crystal is fully ordered then all the atoms of one of these substances (we shall refer to these as 'atoms of the given species') will occupy certain definite lattice points which we shall call 'correct'. In a departure from perfect order, however, some of the atoms will go over to new lattice points, which we shall call 'wrong' (if the solid solution is 'substitutional', then the 'wrong' lattice points are those which would be occupied by atoms of the other species in complete order). Evidently the crystal can become completely ordered only if the numbers of

atoms of each species are equal to the corresponding numbers of 'correct' lattice points. The converse is of course not true, for even if the concentration of the solid solution has the necessary value, the crystal need not be completely ordered.

Let the number of atoms of the given species in the crystal be n, and the number of lattice points which would be occupied by atoms of this species in complete order (i.e. 'correct' lattice points) be n_0; then the crystal can become fully ordered only if $n = n_0$. Further, let l_1 be the number of atoms of the given species which are in 'wrong' places and l_2 the number of lattice points which are not occupied by 'correct' atoms. Then evidently

$$n = n_0 - l_2 + l_1. \tag{72.1}$$

Let c be the concentration of the solid solution defined as the ratio of the number of particles of the given species to the total number, N, i.e.

$$c = n/N. \tag{72.2}$$

The concentration of the fully ordered solution will evidently be

$$c_0 = n_0/N. \tag{72.3}$$

Substituting (72.1) into (72.2) we have

$$N(c - c_0) = l_1 - l_2. \tag{72.4}$$

Thus the concentration of the solid solution is equal to that of the fully ordered solid solution whenever $l_1 = l_2$ (in particular, of course, for $l_1 = l_2 = 0$, which is the condition for complete order). If we introduce the concentrations λ_1 and λ_2 of atoms of the given kind in 'wrong' lattice points, and lattice points not occupied by 'correct' atoms, respectively, defined by

$$\lambda_1 = l_1/N, \qquad \lambda_2 = l_2/N, \tag{72.5}$$

then (72.4) becomes

$$c - c_0 = \lambda_1 - \lambda_2. \tag{72.6}$$

Suppose now that one particle of the given species, occupying a 'wrong' place, goes over into a 'correct' place; l_1 and l_2 will then each be reduced by unity. We can regard the whole crystal as a 'solution' of atoms (of the given kind) in 'wrong' places, and lattice points which are not occupied by the 'correct' atoms, in a 'solvent' consisting of the particles in correct places; l_1 and l_2 will then be the numbers of 'dissolved particles', and λ_1 and λ_2 the concentrations of the 'solution'. Transitions of atoms from 'wrong' places to 'correct'

places can then be considered as 'chemical reactions' between the 'solutes' resulting in formation of the 'solvent'.

If λ_1 and λ_2 are small, i.e. the arrangement of the particles differs only slightly from that of complete order, the law of mass action can be applied to this reaction, in the form deduced for dilute solutions (66.5). In other words λ_1 and λ_2 in the equilibrium state at given p and T, must satisfy the equation

$$\lambda_1 \lambda_2 = K, \tag{72.7}$$

where K is a constant depending on pressure and temperature. The concentration of the 'solvent' formed in this reaction is nearly one, so it can be omitted from the mass action equation.

If $\lambda_1 = \lambda_2 = \lambda_0$, then as we have seen above, the concentration of the solid solution is equal to c_0, that of the fully ordered solid solution. Consequently, we have $K = \lambda_0^2$, where λ_0 is the concentration of particles in wrong places for given pressure and temperature, in a solid solution of concentration c_0. Thus (72.7) becomes

$$\lambda_1 \lambda_2 = \lambda_0^2. \tag{72.8}$$

From (72.6) and (72.8), we obtain λ_1 and λ_2 as

$$\left.\begin{aligned} \lambda_1 &= \tfrac{1}{2}[(c-c_0)+\{(c-c_0)^2+4\lambda_0^2\}^{\frac{1}{2}}], \\ \lambda_2 &= \tfrac{1}{2}[-(c-c_0)+\{(c-c_0)^2+4\lambda_0^2\}^{\frac{1}{2}}]. \end{aligned}\right\} \tag{72.9}$$

These formulae give the concentrations of atoms of the given species occupying 'wrong' places, and lattice points not occupied by the 'correct' atoms, in an almost fully ordered solid solution of given concentration c.

For concentrations of the solid solution such that $(c-c_0)$ is large compared with λ_0, (72.9) is approximately equivalent to

$$\left.\begin{aligned} \lambda_1 &= c-c_0, \\ \lambda_2 &= \lambda_0^2(c-c_0). \end{aligned}\right\} \tag{72.10}$$

In conclusion we may make the following remark. If the composition of the crystal does not correspond to the concentration c_0, it can never be fully ordered; on the other hand, it must become fully ordered at absolute zero (§ 68), since the atoms must then be arranged in a quite definite order. Consequently at sufficiently low temperatures the crystal must break up into two fully ordered different phases.

XII

SURFACE PHENOMENA

73. Surface tension

Two phases in equilibrium must always be separated by a surface of contact, and the existence of this surface gives rise to a number of effects. These effects are, however, much smaller than volume effects, since with an increase of the dimensions of the body the surface area increases slower than the volume; it is because of this that up to now we have always neglected surface effects, since they are of no significance for bulk properties of the body. Nevertheless there are a number of phenomena where it is the surface properties which play the essential role. We should point out that actually phases in contact are separated by a thin transition *layer*, but owing to its extremely small thickness this layer can be considered as a surface.

We shall first of all consider the surface separating two phases of one and the same substance. For a system of two such phases, we have up to now written the thermodynamic identity (for given total volume V) as $dE = T\,dS + \mu\,dN$, where E, S, N are the energy, entropy, and number of particles in the whole system, i.e. the two phases together (the temperature and chemical potential are the same in both phases, so the thermodynamic identity applies to the system as a whole). If now we take account of the surface separating the two phases, we have to allow for the fact that the surface area $\mathfrak{S}$ may change in the course of processes going on in the system, and this means that we must add a term to the thermodynamic identity proportional to the change $d\mathfrak{S}$ of $\mathfrak{S}$, i.e.

$$dE = T\,dS + \mu\,dN + \alpha\,d\mathfrak{S}. \tag{73.1}$$

Evidently $\alpha\,d\mathfrak{S}$ will then be the work in a reversible change of surface area, or

$$dW = \alpha\,d\mathfrak{S}. \tag{73.2}$$

The quantity α is called the *coefficient of surface tension*. It is only possible to speak of this coefficient with reference to a surface of separation between two phases, i.e. when two phases are in equilibrium, and so the coefficient of surface tension has a meaning only on the phase equilibrium curve (which determines the p, T relation, for instance, in equilibrium). Consequently α is a function of only one

(any one) of the thermodynamic quantities describing the system, for instance of p or T.

Comparing $dW = \alpha d\mathfrak{S}$ with $dW = -p dV$ we see that α for a surface is analogous to the pressure for a volume. In particular, it is easy to show that if the surface separating two phases is bounded by some curve, *there will be a force equal to* α, *the surface tension, acting on unit length of this curve, normal to the curve and parallel to the surface.* Since the sign of α in the expression for dW is opposite to that of p in the analogous expression for a change of volume, we see that this force must be directed *into* the boundary curve.

We can no longer use the pressure to characterize the state of a system with two phases in contact, since in the proof of the equality of the pressures of two phases in equilibrium, the dependence of the energy on the surface area was neglected. If this effect is taken into account, the pressures of the two phases may be different, as we shall show later.

Consequently besides the volume we shall use two quantities which have the same values in the two phases, i.e. the temperature and the chemical potential, to describe the state of the system. In addition the surface of separation will be characterized by its area $\mathfrak{S}$. With this set of variables, we now have to use the potential Ω, since this is the thermodynamic potential with respect to the independent variables V, T, μ (see § 46).

The thermodynamic identity for Ω (see (46.9)) may in this case be written as

$$d\Omega = -S dT - N d\mu + \alpha d\mathfrak{S}, \tag{73.3}$$

$d\Omega$ like dE being for constant volume of the system.

For systems of two phases in contact, Ω can be written as a sum of two terms, one of which, Ω_0, is a 'volume' term (i.e. not including the surface, so that Ω_0 is the value of Ω for $\mathfrak{S} = 0$), and the other Ω' takes account of the surface properties. Since Ω is additive, the term Ω' must be proportional to $\mathfrak{S}$, and so by (73.3), Ω' must be equal to $\alpha\mathfrak{S}$. Thus

$$\Omega = \Omega_0 + \Omega' = \Omega_0 + \alpha\mathfrak{S}. \tag{73.4}$$

It was shown in § 46 that the potential Ω tends to a minimum (for processes at constant V, T, μ). Consequently if α were negative, the surface area $\mathfrak{S}$ would tend to become infinite, or in other words the phases would cease to exist separately, since they would mix. We deduce therefore that the coefficient of surface tension is always

positive. Moreover, from the fact that Ω tends to become minimum it follows that the surface area $\mathfrak{S}$ tends to assume the smallest possible value for the given volume. Thus if one phase is immersed in another, it will assume a spherical shape, since a sphere has the smallest surface area for a given volume (this result holds, of course, only for gases and liquids).†

At the point where the two phases become identical, i.e. the critical point, the surface of separation of the phases ceases to exist and α must become zero. From an analysis of the structure of the surface (which we shall not, however, discuss) near the critical point, it can be shown that in this region

$$\alpha \propto (T_c - T)^{3/2}. \tag{73.5}$$

In the case of a surface separating liquid and vapour the law of corresponding states (§ 51) can be applied qualitatively. Its application to surface tension shows that α is the product of a quantity made up of T_c and p_c with the dimensions of a surface tension, i.e. ergs/cm.^{2}, and a function of the dimensionless quantity T/T_c. This gives

$$\alpha = (kT_c p_c^2)^{1/3} f(T/T_c). \tag{73.6}$$

The entropy S of the whole system, like Ω, may also be expressed as the sum of two terms: a volume term S_0 (i.e. the entropy for $\mathfrak{S} = 0$) and a surface term S'.

Remembering that $S = -\partial\Omega/\partial T$ and $\Omega' = \alpha\mathfrak{S}$ we obtain

$$S' = -(\partial\Omega'/\partial T)_{\mathfrak{S}} = -\mathfrak{S}\, d\alpha/dT \tag{73.7}$$

(we write the complete derivative $d\alpha/dT$ since α is a function of only one variable).

Applying the same considerations to the energy of the system, i.e. expressing it as $E = E_0 + E'$, we have that, since $E = \Omega + N\mu + TS$,

$$E' = \Omega' + TS',$$

so that

$$E' = \left(\alpha - T\frac{d\alpha}{dT}\right)\mathfrak{S}. \tag{73.8}$$

† We must, however, bear in mind that these considerations apply only if Ω_0 depends on the volume alone and not on the shape of the phases. This is always so if the system is in no external field, or if the influence of the external field can be neglected (for instance if the volume of one of the phases is very small). If, however, the system is in an external field (of gravity, for instance), the surface area assumes that value for which $\Omega_0 + \alpha\mathfrak{S}$ is minimum.

The quantity of heat absorbed in a reversible change of area from $\mathfrak{S}_1$ to $\mathfrak{S}_2$ (at constant temperature T) is

$$Q = T(S_2'-S_1') = -T\frac{d\alpha}{dT}(\mathfrak{S}_2-\mathfrak{S}_1). \tag{73.9}$$

The sum of the heat Q absorbed and the work $W = \alpha(\mathfrak{S}_2-\mathfrak{S}_1)$ required to carry out the process is, as it should be, equal to the energy change $E_2'-E_1'$.

In conclusion we should point out that if one of the phases is anisotropic, for instance a crystal immersed in some medium, then the surface tension at the different crystal faces will in general be different.

74. Surface pressure

In the proof in § 48, that the pressures of phases in equilibrium must be equal, we neglected (as elsewhere) the effects caused by the surface of separation. If we take account of the fact that displacement of the phase boundary may alter the area of the surface separating the phases, we find that the pressures of the two phases need no longer necessarily be equal. The phase equilibrium condition is then that the temperature and the chemical potentials, but not the pressures of the two phases, should be equal. The difference between the pressures of the two phases is known as the surface pressure.

Let the pressures and volumes of the two phases be p_1, V_1 and p_2, V_2 respectively. Then the 'volume' part Ω_0 (see § 73) of the potential Ω of the whole system (the two phases together) will be $-(p_1V_1+p_2V_2)$ since the potentials for the two phases are $-p_1V_1$ and $-p_2V_2$ (by (46.8)). Substituting this into (73.4) we have

$$\Omega = -p_1V_1-p_2V_2+\alpha\mathfrak{S}. \tag{74.1}$$

The potential Ω tends to a minimum in processes at constant volume, temperature, and chemical potential, and in the case of a two-phase system this means that Ω tends to a minimum for transitions from one phase to the other, in which the total volume V_1+V_2 and the temperature and chemical potential remain constant. Thus in equilibrium Ω has a minimum with respect to such processes, i.e. $d\Omega = 0$, under the conditions $T =$ const., $\mu =$ const. and V_1+V_2 $=$ const.

The differential $d\Omega$ can be found from (74.1), but it must be remembered that p_1 and p_2 are the pressures of two phases in equilibrium, so that they satisfy the equations $\mu_1(p_1, T) = \mu_2(p_2, T) = \mu$,

where μ is the common value of the chemical potentials of the two phases. Hence p_1 and p_2 can be considered as functions of T and μ, and since we want the condition for Ω to be a minimum at constant T and μ, p_1 and p_2 and also μ must be treated as constants in differentiating the equation (74.1). We thus obtain

$$d\Omega = -p_1 dV_1 - p_2 dV_2 + \alpha\, d\mathfrak{S} = 0,$$

and since $dV_1 + dV_2 = 0$, this becomes

$$d\Omega = -dV_1(p_1 - p_2) + \alpha\, d\mathfrak{S} = 0, \tag{74.2}$$

and hence

$$p_1 - p_2 = \alpha\, d\mathfrak{S}/dV_1. \tag{74.3}$$

Now it can be shown by differential geometry that the derivative $d\mathfrak{S}/dV_1$ is given by

$$\frac{d\mathfrak{S}}{dV_1} = \frac{1}{r_1} + \frac{1}{r_2}, \tag{74.4}$$

where r_1 and r_2 are the principal radii of curvature at the given point. The radii r_1 and r_2 in this formula are counted positive if they are directed into the first phase. If we put $d\mathfrak{S}/dV_2$ instead of $d\mathfrak{S}/dV_1$ in (74.4), we should have to take the opposite signs for r_1 and r_2, i.e. they would be counted positive if the radii were directed into the second phase.

Substituting (74.4) into (74.3) we find

$$p_1 - p_2 = \alpha\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \tag{74.5}$$

which gives the difference of pressure of the two phases at any point on their surface of separation. In the case of a plane surface of separation, r_1 and r_2 are both infinite, and the pressures of the two phases are equal.

If one of the phases, say the first, is a sphere immersed in the second phase, then the surface of separation is spherical and its principal radii of curvature are equal to each other, and have the same value (the radius r of the sphere) at all points of the surface. Equation (74.5) then becomes

$$p_1 - p_2 = 2\alpha/r. \tag{74.6}$$

This result can also be obtained directly from (74.3), if we remember that in this case $\mathfrak{S} = 4\pi r^2$, $V_1 = \frac{4}{3}\pi r^3$, so that $d\mathfrak{S} = 8\pi r\, dr$, $dV_1 = 4\pi r^2 dr$, so that $(d\mathfrak{S}/dV_1) = 2/r$.

Equations (74.5, 6) give only the difference of pressures in the

two phases and we shall now calculate the two separate pressures. If the surface of separation were plane, we have seen that the pressures would be equal; we denote their common value in this case by p_0, and let

$$\delta p_1 = p_1 - p_0, \qquad \delta p_2 = p_2 - p_0.$$

δp_1 and δp_2 then represent the changes of pressures due to the curvature of the surface (p_1 and p_2 refer, of course, to the same temperature as p_0, since we are considering the influence of curvature at given constant temperature).

Let μ_1 and μ_2 be the chemical potentials of the two phases; then since the phases are in equilibrium, $\mu_1 = \mu_2$ for any form of the separation surface. Differentiating this equation with respect to the curvature of the surface at constant temperature and using (43.12) we obtain

$$v_1 \delta p_1 - v_2 \delta p_2 = 0. \tag{74.7}$$

The changes δp_1 and δp_2 have been assumed small (which is justified by the insignificance of surface effects), and v_1 and v_2 are the volumes per particle of the first and second phases respectively.

Combining (74.7) with (74.5), which can be written as

$$\delta p_1 - \delta p_2 = \alpha\left(\frac{1}{r_1} + \frac{1}{r_2}\right),$$

we obtain the following expressions for δp_1 and δp_2:

$$\left.\begin{aligned} \delta p_1 &= \frac{v_2 \alpha}{v_2 - v_1}\left(\frac{1}{r_1} + \frac{1}{r_2}\right), \\ \delta p_2 &= \frac{v_1 \alpha}{v_2 - v_1}\left(\frac{1}{r_1} + \frac{1}{r_2}\right). \end{aligned}\right\} \tag{74.8}$$

We shall now examine in more detail the case where one of the phases (the second) is gaseous, and the other is liquid, and has moreover a spherical shape (a drop). Since the volume per particle of a gas is always much greater than that of a liquid, we can neglect v_1 in comparison with v_2, and also since the liquid is spherical, $r_1 = r_2 = r$, we have

$$\left.\begin{aligned} \delta p_1 &= 2\alpha/r, \\ \delta p_2 &= 2v_1 \alpha/v_2 r. \end{aligned}\right\} \tag{74.9}$$

Applying Clapeyron's equation, $v_2 = kT/p_2$ (i.e. assuming the gas to be perfect), we find for the gas pressure

$$\delta p_2/p_0 = 2v_1 \alpha/kTr \tag{74.10}$$

(since p_2 in the denominator can be put approximately equal to p_0).

Thus we see that the vapour pressure over a liquid drop decreases with increasing radius of the drop; it has its lowest possible value for a plane surface ($r = \infty$).

Instead of determining the differences δp_1 and δp_2 of pressure for a curved and a plane surface at the same temperature, we can determine the differences

$$\delta T_1 = T_1 - T_0, \qquad \delta T_2 = T_2 - T_0,$$

where T_0 is the common temperature of the two phases in equilibrium

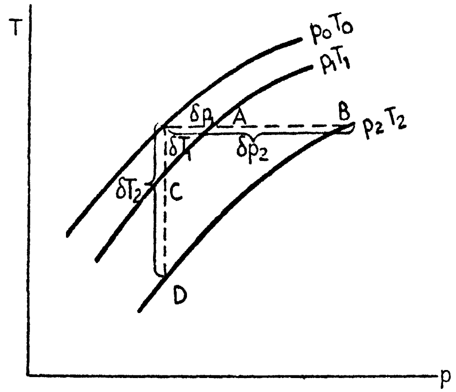


FIG. 54.

at some given pressure and with a plane surface of separation, and T_1 and T_2 are the temperatures of the two phases, when each has the same given pressure, but a curved surface of separation (the two phases will then *not* be in equilibrium; see below).

Suppose for instance that the upper curve in Fig. 54 is the phase equilibrium curve for a plane separation surface, so that each point on it gives corresponding values of p_0 and T_0 for phase equilibrium. If the surface of separation is curved, then the pressures of the two phases for a given temperature are no longer equal, and the states of the two phases are represented by two separate curves (the lower two curves in Fig. 54).

The differences δp_1, δp_2, δT_1, δT_2 are then as shown by the dotted lines. It should be noticed that although the points A and B represent states of the two phases in equilibrium with each other, the states represented by C and D will *not* correspond to phase equilibrium.

Assuming the differences δp_1, δT_1, etc., to be small we can express

them in terms of each other by means of the Clapeyron-Clausius equation (49.3). We have, however, to change the sign in this equation as can be seen from Fig. 54, since dp/dT is positive along the curves of Fig. 54, while δT_1 and δp_1 (or δT_2 and δp_2), as defined here, have opposite signs. We thus find

$$\delta p_1 = \frac{q\,\delta T_1}{T_0(v_1-v_2)}, \qquad \delta p_2 = \frac{q\,\delta T_2}{T_0(v_1-v_2)}, \tag{74.11}$$

where q is the heat of transition (per particle) from the first into the second phase. Substituting these equations into (74.8) we obtain

$$\left.\begin{aligned} \delta T_1 &= -\frac{v_2 T_0 \alpha}{q}\left(\frac{1}{r_1}+\frac{1}{r_2}\right), \\ \delta T_2 &= -\frac{v_1 T_0 \alpha}{q}\left(\frac{1}{r_1}+\frac{1}{r_2}\right). \end{aligned}\right\} \tag{74.12}$$

75. Formation of nuclei

If a substance is in a metastable state (§§ 35, 48) it will sooner or later go over from this state into a stable one; for instance a supercooled vapour will in the course of time condense into a liquid, a supercooled liquid will eventually become a solid, and a superheated liquid will eventually evaporate into a gas. This transition takes place in the following way. Owing to fluctuations in a uniform phase small amounts ('aggregations') of the other phase will form (for instance drops of liquid in a vapour), but if the first phase is stable these 'drops' of the other phase must be unstable and will eventually disappear again. If, however, the main phase is metastable, then for a sufficient size of the aggregations of the other phase (formed by fluctuations) this other phase will be more stable than the initial one. In this case the drops of the other phase do not disappear, but continue to grow, becoming as it were centres of transition from the metastable to the stable phase. For instance the liquid drops in the supercooled vapour, if sufficiently large, become centres of condensation of the vapour.

For each metastable phase there is a minimum size, which the aggregation of the other phase (formed by fluctuations) must have in order to be more stable than the initial phase. For smaller sizes than this minimum the main phase remains more stable than the other one and the aggregations of the other phase disappear again. Such aggregations of the other phase, having the requisite minimum size, are called *nuclei* of growth of this phase.

Since one or the other phase is more stable, according as the aggregations are smaller or larger than the nuclear size, the nuclei themselves must be in unstable equilibrium with the initial phase. Thus aggregations of sizes larger than that of a nucleus, continue to grow until the metastable phase has completely transformed into the stable one.

The nucleus can be taken as spherical, since its surface area tends to a minimum (this does not, of course, apply to nuclei of crystals), and if its radius is r, the equilibrium condition is $p'-p = 2\alpha/r$ (by (74.6)), so that

$$r = 2\alpha/(p'-p) \tag{75.1}$$

(quantities with a dash refer to the nucleus, while those without refer to the surrounding metastable phase).

We shall now calculate the probability of the formation of a nucleus. In other words we must find the probability of a fluctuation in which a spherical aggregation of the other phase forms with a radius given by (75.1). We know from § 40 (equation (40.1)) that the probability of such a fluctuation is proportional to $e^{-W/kT}$, where W is the minimum work necessary to form the nucleus and T is the temperature of the medium (in the present case, the metastable phase); this is also the temperature of the nucleus.

Since the temperature and chemical potential of the nucleus are equal to those of the medium the minimum work necessary to form the nucleus is equal to the difference of the potential Ω after and before its formation. Before formation of the nucleus the volume of the metastable phase was $V+V'$ and its potential $\Omega = -p(V+V')$; after formation the potential Ω becomes $-pV-p'V'+\alpha\mathfrak{S}$, hence the change of Ω, i.e. the work W, is given by

$$W = -(p'-p)V'+\alpha\mathfrak{S}. \tag{75.2}$$

Since the nucleus is spherical, $V' = \frac{4}{3}\pi r^3$ and $\mathfrak{S} = 4\pi r^2$, so putting in the value of r from (75.1), we find

$$W = \tfrac{16}{3}\pi\alpha^3/(p'-p)^2. \tag{75.3}$$

Consequently the probability that the nucleus will be formed is

$$w \propto \exp[-16\pi\alpha^3/3kT(p'-p)^2]. \tag{75.4}$$

As in the previous section let p_0 denote the common pressure of the two phases when their surface of separation is plane, and let $p-p_0 = \delta p$, $p'-p_0 = \delta p'$. If the main phase is only slightly superheated or supercooled, then δp_1 and δp_2 are small, and we find analogously to (74.7)

$$v'\,\delta p' - v\,\delta p = 0, \tag{75.5}$$

where v' and v are the volumes of the nucleus and the metastable phase per particle.

Now in equation (75.4) we can write $(\delta p' - \delta p)$ instead of $p' - p$, and expressing $\delta p'$ in terms of δp from (75.5) we obtain the probability of formation of a nucleus in a slightly superheated or supercooled phase

$$w \propto \exp\left(\frac{-16\pi\alpha^3 v'^2}{3kT(v-v')^2(\delta p)^2}\right). \tag{75.6}$$

We shall consider some special cases of this result. Suppose first of all that the metastable phase is a superheated liquid in which nuclei of the gaseous phase are formed, i.e. bubbles of vapour. Since the volume per particle of the vapour is much greater than that of the liquid, v can be neglected in comparison with v' in (75.6) and we obtain

$$w \propto \exp\{-16\pi\alpha^3/3kT(\delta p)^2\}. \tag{75.7}$$

For the formation of nuclei (drops) of liquid in a supercooled vapour v' can be neglected in comparison with v (in $(v-v')$ of (75.6)), and for v we can use Clapeyron's equation (assuming the vapour to be a perfect gas), i.e. we can put $v = kT/p \simeq kT/p_0$; this gives

$$w \propto \exp\left(\frac{-16\pi\alpha^3 v'^2 p_0^2}{3(kT)^3(\delta p)^2}\right). \tag{75.8}$$

If $\delta p/p$ is not small this formula cannot be used, since the volume of a vapour depends strongly on its pressure, and the approximations made will be invalid; we then have to use the general formula (75.4). To find $(p'-p)$ we must remember that p' and p satisfy the equation $\mu'(p', T) = \mu(p, T)$, while the common pressure p_0 of gas and liquid with a plane separation surface is given by $\mu'(p_0, T) = \mu(p_0, T)$. Subtracting this equation from the previous one we obtain

$$\mu'(p', T) - \mu'(p_0, T) = \mu(p, T) - \mu(p_0, T).$$

For the liquid, on account of its small compressibility, the change of pressure $p'-p_0$ has no significant effect, so the left-hand side of the equation can be expanded in a power series, the first term of which is $(p'-p_0)v'$. The chemical potential of the vapour, on the other hand, is $\mu = kT\log p + \chi(T)$, so the last equation becomes

$$\delta p' = p' - p_0 = (kT/v')\log(p/p_0).$$

It is evident from (75.5) that $\delta p' \gg \delta p$, so this equation can be written as

$$p' - p = (kT/v')\log(p/p_0)$$

and substitution into (75.4) now gives

$$w \propto \exp\left(\frac{-16\pi\alpha^3 v'^2}{3(kT)^3[\log(p/p_0)]^2}\right). \tag{75.9}$$

For small values of $\delta p/p$ this formula becomes equivalent to (75.8).

Finally, in the equations (75.6–8) we can introduce $\delta T = T - T_0$ instead of δp, where T is the temperature of the metastable phase (with which the nucleus is in equilibrium) and T_0 is the phase equilibrium temperature for a plane separation surface (thus δT gives the 'degree' of superheating of the metastable phase). As in the previous section (equation (74.10)) we have

$$\delta p = q\,\delta T/T_0(v-v'), \tag{75.10}$$

where q is the heat of transition per particle, from the metastable phase to the phase of the nucleus. Substituting (75.10) into (75.6) we find the probability of formation of a nucleus in a superheated phase as

$$w \propto \exp\left(\frac{-16\pi\alpha^3 v'^2 T_0}{3q^2k(\delta T)^2}\right) \tag{75.11}$$

(δT is assumed small, so that T can be replaced by T_0).

The formulae deduced in this section remain qualitatively true also for the formation of nuclei of an anisotropic phase (crystals). Such nuclei no longer have a spherical form, since their surface pressures are different on different faces (see § 73); the shape of the nucleus is then determined by the condition that the sum of the products of the coefficients α and the surface areas of the various faces should be a minimum. Thus the numerical factors in the above formulae will for this case have different values.

76. The growth of crystals

We shall now discuss the process of crystal growth. This consists in the formation of new layers of the crystal lattice, on the surface of a crystal immersed in a supercooled liquid phase of the same substance. A similar process takes place with a crystal immersed in a supersaturated solution, but we shall discuss only the first case here.

If a molecule of the liquid settles on the crystal surface, then this molecule, which begins the formation of a new layer in the lattice, will be in conditions quite different from those of the other molecules in the crystal (this does not happen, of course, in liquid bodies). Consequently the system of the crystal and one or more molecules

settled on its surface will in general be unstable, and further growth of the crystal immersed in the liquid will take place, quite analogously to the formation of nuclei of one phase in another. Thus, owing to fluctuations, small regions of the next lattice layer may be formed on the crystal surface. If, however, these regions are sufficiently small they will be unstable and will eventually return to the liquid phase. In order that these regions should be able to serve as centres for the formation of a new layer, it is necessary that their further growth should be more probable than their return to the liquid. This will happen if the size of such a region is sufficiently large, and we shall now determine the probability of formation of a region with the minimum size necessary for further growth (i.e. the probability of formation of a nucleus).

Just as in the case of two contiguous phases an extra term $\alpha\mathfrak{S}$ had to be added to the Gibbs free energy to take account of the surface of separation, so in the formation of part of a new layer on a crystal surface, we have to add a term proportional to the linear dimensions of this region (e.g. its perimeter) to the Gibbs free energy G. The coefficient in this term can be called the 'linear tension' (by analogy with surface tension). On account of the anisotropy of the crystal, however, the form of this term depends in general on the shape of the region, and also on the face of the crystal on which it is formed. For our purposes it will be sufficient to express this extra term in the form $2\beta\sqrt{n}$, where 2β is some constant, and n the number of molecules in the region formed in the new layer. The change in Gibbs free energy of the whole system for formation of the region will be

$$\Delta G = 2\beta\sqrt{n}+(\mu'-\mu)n, \tag{76.1}$$

where μ' and μ are the chemical potentials of the crystal and the liquid respectively.

Now G, as we know, tends to a minimum, i.e. ΔG tends to diminish, and consequently the region formed will be unstable as long as an increase of the number of molecules, n, in it causes an increase of ΔG. Thus the size of the nucleus is determined by the condition that ΔG has a maximum, so that the number of molecules in it is determined by the equation

$$\frac{\partial \Delta G}{\partial n} = \frac{\beta}{\sqrt{n}}+(\mu'-\mu) = 0,$$

or

$$n = \beta^2/(\mu-\mu')^2. \tag{76.2}$$

The probability w of a fluctuation is proportional to $e^{-W/kT}$, and W, the minimum work necessary to form the region in a new layer, is equal to ΔG, since the pressure and temperature are constant; so substituting for n from (76.2) into (76.1) we find

$$w \propto \exp[-\beta^2/(\mu-\mu')kT]. \qquad (76.3)$$

Let δT be the degree of supercooling of the liquid, i.e. the difference between the temperature T and the temperature T_0 for phase equilibrium of the liquid and solid at the given pressure. Similarly to our procedure in § 74 (in the deduction of (74.7) for instance), we expand $\mu-\mu'$ in powers of δT (which is assumed small), and retaining only the first term we have

$$\mu-\mu' = \delta T(s-s'),$$

where s and s' are the entropies per molecule of liquid and crystal respectively (the term $\mu(T_0)-\mu'(T_0)$ vanishes because $\mu'(T_0) = \mu(T_0)$ is the condition for phase equilibrium at temperature T_0). Substituting $q = T(s-s')$, where q is the latent heat of transition per molecule from solid to liquid, we obtain

$$\mu-\mu' = q\,\delta T/T$$

and (76.3) becomes

$$w \propto \exp(-\beta^2/qk\,\delta T). \qquad (76.4)$$

77. Adsorption

In the previous sections of this chapter we have discussed the surfaces of separation between two phases of one and the same substance. We shall now consider the case of two phases in contact, each of which is a solution of the same solute in two different phases of a solvent; all the quantities will refer to a given quantity of the solvent. Let the number of particles of the solute be $n = n_0+n'$, where n_0 is the total number of solute molecules there would be if $\mathfrak{S} = 0$, i.e. if there were no separation surface (or, more correctly, no transition layer). The number n_0 defined in this way may be either less or greater than n. Now $n' = n_0-n$ is evidently the difference between the number of particles in the transition layer and the number of particles which would be there if the concentration of the transition layer was the same as in the bulk of the solution. If $n > n_0$, then $n' > 0$, which means that the solute is relatively more concentrated in the surface layer (*positive adsorption*), while if $n < n_0$, then $n' < 0$ and the concentration of the solute in the surface layer is less than in the bulk of the solution (*negative adsorption*).

Since the negative derivative of the potential Ω with respect to the chemical potential gives the number of particles, and since $\Omega' = \alpha\mathfrak{S}$ (see (73.4)), we have

$$n' = -\partial\Omega'/\partial\mu = -\mathfrak{S}(\partial\alpha/\partial\mu)_T. \tag{77.1}$$

This equation gives the number of solute particles adsorbed in the surface layer between the two phases.

Since $(\partial\alpha/\partial\mu)_T = (\partial\alpha/\partial n)_T(\partial n/\partial\mu)_T$ and $(\partial n/\partial\mu)_T$ is always positive (see (59.5)), $(\partial\alpha/\partial\mu)_T$ and $(\partial\alpha/\partial n)_T$ have the same sign, and so (77.1) shows that *a solute which increases the surface tension* (i.e. one for which α increases with n) *is adsorbed negatively*, while *solutes which lower the surface tension are adsorbed positively*.

For dilute solutions the expression $\mu = kT\log c + \psi(p, T)$ can be substituted for the chemical potential in (77.1) (c is the concentration in either phase; it does not matter which, since the concentrations are proportional to each other (see § 56)). This gives

$$n' = -\frac{\mathfrak{S}c}{kT}\frac{\partial\alpha}{\partial c}. \tag{77.2}$$

A similar equation with p substituted for c is obtained for the adsorption of a perfect gas. For weak adsorption in dilute solutions α can be expanded in powers of c, giving approximately $\alpha = \alpha_0 + \alpha_1 c$, where α_0 is the surface tension of the pure solvent. Substituting into (77.2) we have

$$\alpha_1 = -n'kT/\mathfrak{S}c,$$

and consequently

$$\alpha = \alpha_0 - n'kT/\mathfrak{S}. \tag{77.3}$$

It will be noticed that this result has a formal resemblance to Clapeyron's equation.

The minimum work W which has to be spent in adsorption at constant pressure is equal to the change of the potential Ω, i.e.

$$W = \mathfrak{S}(\alpha - \alpha_0). \tag{77.4}$$

Using (17.19) we can now find Q, the *heat of adsorption*:

$$Q = \mathfrak{S}[(\alpha - \alpha_0) - T\partial(\alpha - \alpha_0)/\partial T]. \tag{77.5}$$

78. Two-dimensional and one-dimensional systems

In the same way that different phases can exist in bulk matter, it is possible to have different phases in a surface layer. In other words the state of the surface layer may change abruptly (for a continuous variation of the temperature, for instance), and in suitable conditions the surface layer may consist of two contiguous phases separated by

some curve in the surface. It is easy to see that for two such contiguous phases the surface tensions must be equal:

$$\alpha_1 = \alpha_2 \tag{78.1}$$

(this is evident from a consideration of the forces at the boundary curve separating the two phases). The latent heat of transition Q (for a given area $\mathfrak{S}$) is $Q = T(S_2-S_1)$, or, using (73.7),

$$Q = T\mathfrak{S}\left(\frac{d\alpha_1}{dT}-\frac{d\alpha_2}{dT}\right). \tag{78.2}$$

If one (or both) of the phases of the body are anisotropic, then evidently their surface of separation will also be anisotropic. In principle it is also possible to have an anisotropic surface separating two isotropic phases.† It can be shown in this case that such anisotropic surfaces are always analogous to liquid crystals, and that no surface analogue of a solid crystal can exist.

One-dimensional systems (i.e. in which all the particles are close to some curve) differ fundamentally from two- and three-dimensional systems, however, and in particular it can be shown that *it is impossible for different phases to exist in a one-dimensional system.*

Thus, suppose that a one-dimensional system does consist of two phases in contact (at some point on the curve), then it is easy to see that the two phases will tend to mix with each other in such a way that the curve will consist of a number of alternating sections of the two phases. A system of this kind can be considered as a 'solution' of the points of contact of the various sections in the two phases. If this 'solution' is dilute, we can use the expression for the chemical potential of a dissolved substance, i.e.

$$\partial G/\partial n = kT\log c+\psi(p, T),$$

where n is the number of 'dissolved' points of contact and c their 'concentration'. For small concentrations, $\log c$ has a large negative value, so that $\partial G/\partial n$ is negative. In other words G decreases with increase of n, and since G tends to a minimum, n must tend to increase (until, of course, $\partial G/\partial n$ becomes positive). This proves the above statement that no phases can exist in a one-dimensional system, since if they did exist, they would always tend to mix with each other.

† Such cases are apparently sometimes observed.

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